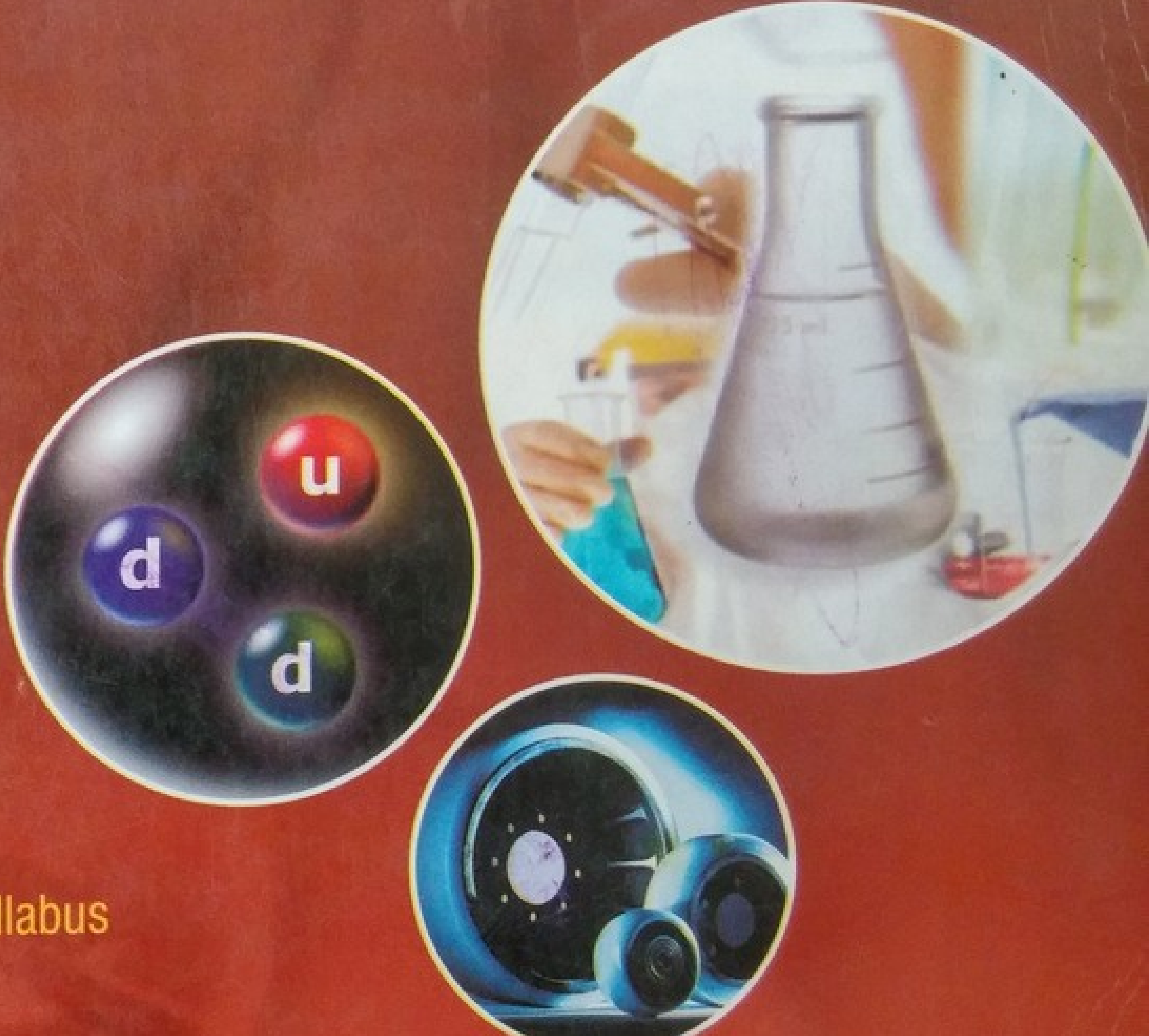
7th Edition

KIPS

ENTRY TEST SERIE

For All Kinds of Entry & Aptitude Tests

CHEMISTRY



- Quick Review of the Syllabus
- Highlighted Points
- Mind Map for every Chapter
- Hundreds of Practice Questions
- Diagnostic Test
- Sample Paper for Entry Test
- Chapter-Wise Exercises with Answer Keys

A KIPS Publicati

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Diagnostic Test a

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KIPS DIAGNOSTIC TEST

- This diagnostic test is designed to help you to pinpoint the weak areas in your background Sit aside 1 hour to take this test. Check your answers with those at the end of the test. Then evaluate yourself.

MCAT/ECAT

Note:- Chemistry paper of ECAT contains 30 questions while MCAT contains 60 questions, so extra questions have been added in the sample paper.

1. Isotopes differs in
   (a) arrangement of electrons in orbitals (b) position in the periodic table
   [✓ (c) properties depend upon mass] (d) chemical properties
2. The mass of one mole of electron is
   (a) 1.008 mg [✓ (b) 0.55 mg]
   (c) 0.184 mg (d) 1.637 mg

1 — 9.01×10^{-31} kg
$9.01 \times 10^{-31} \times 6.02 \times 10^{23}$
54×10^{-8}
$= 55 \times 10^{-5}$
$= 55 \times 10^{-2}$
.55

3. The volume occupied by 1.4g CO at S.T.P is
   (a) 22.4 dm^3 (b) 2.24 dm^3
   (c) 1.12 cm^3 [✓ (d) 1.12 dm^3]

.05
1 — 22.4
0.05×22.6

4. The number of atoms in a molecule determines
   (a) micromolecule (b) macromolecule
   (c) molecularity [✓ (d) atomicity]
5. Which of the following set has all species isoelectronic
   (a) F^-, Cl^-, Br^- (b) Li^{+1}, Na^{+1}, k^{+1}
   [✓ (c) F^-, Ne, Na^+] (d) H^+, H^-, H
6. Which element has same isotopes like palladium
   (a) Nickel [✓ (b) Calcium]
   (c) Cadmium (d) Tin
7. Water absorber used in combustion analysis is
   (a) 50% KOH (b) Lime water
   (c) $CaCl_2$ [✓ (d) $Mg(ClO_4)_2$]
8. A limiting reactant is one which
   (a) is taken in lesser quantity in grams as compared to other reactants
   (b) is taken in lesser quantity in volume as compared to other reactants
   (c) gives the maximum amount of the product which is required
   [✓ (d) gives the minimum amount of the product under consideration.]
9. The type of filtering media used for filtration depending upon.
   (a) Nature of reactants (b) Nature of crucible
   (c) Nature of product [✓ (d) Nature of precipitate.]
10. A safe and more reliable method for drying the crystal is
    (a) Hot air currents (b) Folds of filter paper
    (c) Oven [✓ (d) Vacuum desiccator.]

11. A method of separation of components from its solution using Distribution law is
(a) Sublimation (b) Crystallisation
(c) Solvent extraction (d) Distillation

12. A real gas obeying vander waal's equation will resemble the ideal gas if
(a) Both 'a' and 'b' are small (b) Both 'a' and 'b' are large
(c) 'a' is small and 'b' is large (d) 'a' is large and 'b' is small.

13. Equal masses of methane and oxygen are mixed in empty container at 250°(C) The fraction of total pressure exerted by oxygen is
(a) 1/17 (b) 16/17
(c) 1/3 (d) 2/3

14. Plasma is used in
(a) Fluorescent bulb (b) Neon signs
(c) Lasers (d) All of these

15. The molecules of CO_2 in dry ice form
(a) Ionic crystal (b) Covalent crystal
(c) Molecular crystal (d) Any type of crystal

16. Which of the following is pseudo solid
(a) CaF_2 (b) NaCl
(c) Glass (d) Diamond

17. Only London dispersion forces are present among the
(a) Molecules of water in liquid state
(b) Atoms of helium in gaseous state at high temperature
(c) Molecules of hydrogen chloride gas
(d) Molecules of solid iodine

18. Bohr's model is contradicted by
(a) Planck's theory (b) Dual nature of matter
(c) Heisenberg's uncertainty principle (d) All of these

19. Quantum number values for 3p orbitals are
(a) $n=3 \quad l=2$ (b) $n=3 \quad l=0$
(c) $n=3 \quad l=1$ (d) $n=3 \quad l=3$

20. When fast neutron strike the nucleus of nitrogen the particles ejected are
(a) α - particles (b) β - particles
(c) γ - rays (d) X – rays

21. Which specie has unpaired electrons in antibonding molecular orbitals
(a) O_2^{+2} (b) N_2^{-2}
(c) B_2 (d) O_2^{-2}

22. Atomic radius can be determined by
(a) X – ray diffraction (b) Spcetrophotometer
(c) Optical microscope (d) Electron microscope

23. For a given process the heat changes at constant pressure (q_p) and at constant volume (q_v) are related to each other as
(a) $q_p = q_v$ (b) $q_p < q_v$
(c) $q_p > q_v$ (d) $q_p = q_v/2$

24. For which system does the equilibrium constant Kc has unit of (concentration)$^{-1}$
(a) $N_2+3H_2 \rightleftharpoons 2NH_3$ (b) $H_2+I_2 \rightleftharpoons 2HI$
(c) $2NO_2 \rightleftharpoons N_2H_4$ (d) $PCl_5 \rightleftharpoons PCl_3+Cl_2$

25. Solubility product of AgCl is 2.0 x 10^{-10} mol^2 dm^{-6}. Maximum Concentration of Ag^{+1} ions in the solution is
(a) 2.0 x 10^{-10} mol dm^{-3} (b) 1.414 x 10^{-5} mol dm^{-3} ✓ S^2
(c) 1.0 x 10^{-10} mol dm^{-3} (d) 1.0 x 10^{-5} mol dm^{-3}

26. 18g glucose is dissolved in 90g water the relative lowering in vapour pressure is equal to
(a) $\frac{1}{5}$ (b) 5.1
(c) 6 (d) $\frac{1}{51}$ •

$\frac{\Delta P}{P^{\circ}} = x_2$ $\frac{0.1}{0.1+5} = \frac{0.1}{5.1} =$

27. Which of the following solution has the highest boiling point?
(a) 5.85 % NaCl Solution • (b) 18.0 % glucose solution
(c) 6.0 % urea solution (d) All have same boiling point

28. Stronger is the oxidizing agent greater is the
(a) Oxidation potential (b) Redox potential •
(c) e.m.f of cell (d) standard reduction potential ✓

29. Which of the following can be used in laptops?
(a) Silver oxide battery (b) Fuel cell
(c) Nickel cadmium cell • (d) Lead accumulator

30. Which is true about Zn-Cu galvanic cell?
(a) Reduction occurs at anode
(b) K^+ ion transfer from salt bridge to left beaker of $ZnSO_4$
(c) Oxidation occurs at cathode
(d) Anode is negatively charged •

31. Which is the unit of (K) rate constant for zero order reaction? [illegible]
(a) s^{-1} • (b) mol dm^{-3} s^{-1} ✓
(c) mol^{-1} dm^3 s^{-1} (d) mol^{-2} dm^6 s^{-1}

32. Nitrates of which pair gives different products on thermal decomposition
(a) Na, K (b) Mg, Ca
(c) Li, Na • (d) Li, Ca

33. Which is carnalite
(a) KCl (b) NaCl
(c) KCl. $MgCl_2.6H_2O$ • (d) Na_2CO_3. $10H_2O$

34. Keeping in view the size of atom, which is in correct order
(a) Mg > Sr (b) Ba > Mg
(c) Lu > Ce (d) Cl > I •

35. Which one does not give borax bead test
(a) Copper sulphate (b) Barium sulphate △
(c) Cobalt sulphate (d) Nickel sulphate

36. Which one is not the use of silicones
(a) Lubricant (b) Water repellent film
(c) Rubber sheet (d) Medicine •

37. The most reactive allotropic form of phosphorus is
(a) White △ (b) Red
(c) Black (d) Violet

38. Chemical composition of cinnabar is
(a) FeS_2 (b) HgS •
(c) PbS (d) ZnS

39. Which molecule has the highest bond energy among the halogens
(a) Fluorine
[✓ (b) Chlorine]
(c) Iodine
(d) Bromine

40. When chlorine is passed through hot solution of caustic soda the reaction is said as
(a) Displacement
(b) Reduction
(c) Disproportionation reaction
(d) Double displacement reaction

41. The most paramagnetic element is
[✓ (a) Iron]
(b) Cobalt
(c) Chromium
(d) Manganese

42. In the complex $[Cr(OH)_3(H_2O)_3]$ the coordination number is
(a) 2
(b) 3
(c) 4
[✓ (d) 6]

43. Which one of the following looks odd
(a) H_2SO_4
(b) $KMnO_4$
[✓ (c) H_2S]
(d) K_2CrO_4

44. A great variety of the organic compounds is due to its property of carbon
(a) Show tetravalency
[✓ (b) Exhibit catenation]
(c) Show isomerism
(d) Can form multiple bonds

45. In 1- pentene -4- yne the carbon exhibit hybridization
(a) $sp^3 - sp^2$
(b) $sp^2 - sp$
(c) $sp^2 - sp$
[✓ (d) $sp^3 - sp^2 - sp$]

$C=C-C-C\equiv C$

46. Vinyl acetylene combines with hydrochloric acid produces
(a) Divinyl acetylene
(b) Ethylidine dichloride
[✓ (c) Chloroprene]
(d) 1,3,3, trichloro butane

47. When benzene is heated in air with V_2O_5 at 450°C yields
(a) Phenol
[✓ (b) Maleic anhydride]
(c) Glyoxal
(d) Benzoic acid

48. When toluene reacts with chlorine in sunlight, the first major product is
[✓ (a) Benzyl chloride]
(b) Benzal dichloride
(c) O-chlorotoluene
(d) O-chlorotoluene and P-chlorotoluene

49. Which one of the following will be sulphonated readily?
(a) Chlorobenzene
[✓ (b) Toluene]
(c) Nitrobenzene
(d) Benzene

50. Which one of the following is not a good leaving group?
(a) HSO_4^-
[✓ (b) Cl^-]
(c) OH^-
(d) Br^-

51. When CO_2 is made to react with ethyl magnesium iodide in dry ether followed by acid hydrolysis yields
(a) Carboxylic acid
(b) Ethanoic acid
[✓ (c) Propanoic acid]
(d) Butanoic acid

52. The process of fermentation involves all the enzymes except
(a) Diastase
(b) Invertase
(c) Zymase
[✓ (d) Sucrase]

53. Ethyl chloride on reduction in the presence of Zn/HCl produces
(a) n. butane
(b) Ethanol
[✓ (c) Ethane]
(d) Diethyl ether

$C_2H_5Cl + Zn + HCl$

54. Which one does not exhibit aldol condensation
(a) Ethanal
(b) Acetone
[✓ (c) Benzaldehyde]
(d) Butanone

55. For industrial preparation of CH_3CHO catalytic promoter is
(a) $PdCl_2$ (b) Cu_2Cl_2 △
(c) $CuCl_2$ (d) $PbCl_2$

56. The common name of propane -1,3-dioic acid is
(a) Oxalic acid (b) Succinic acid
(c) Malonic acid • (d) Fumaric acid

C – COOH
|
C
|
C – COOH

57. Which of the following is not a fatty acid?
(a) Propanoic acid (b) Acetic acid
(c) Phthalic acid • (d) Butanoic acid

58. Industrial materials, thermal power stations are coated with
(a) Polyester resins (b) Epoxy paints △
(c) polyamide resins (d) Polyvinyl chloride

59. Which one of the following fertilizers provides the nitrogen and phosphorus to the plant?
(a) Urea (b) Calcium superphosphate
(c) Diammonium phosphate • (d) Potassium nitrate

60. Chlorination of water may be harmful if the water contains
(a) Ammonia △ (b) Dissolved oxygen
(c) Carbon dioxide (d) All

W = 10

UA = 6

ttcl

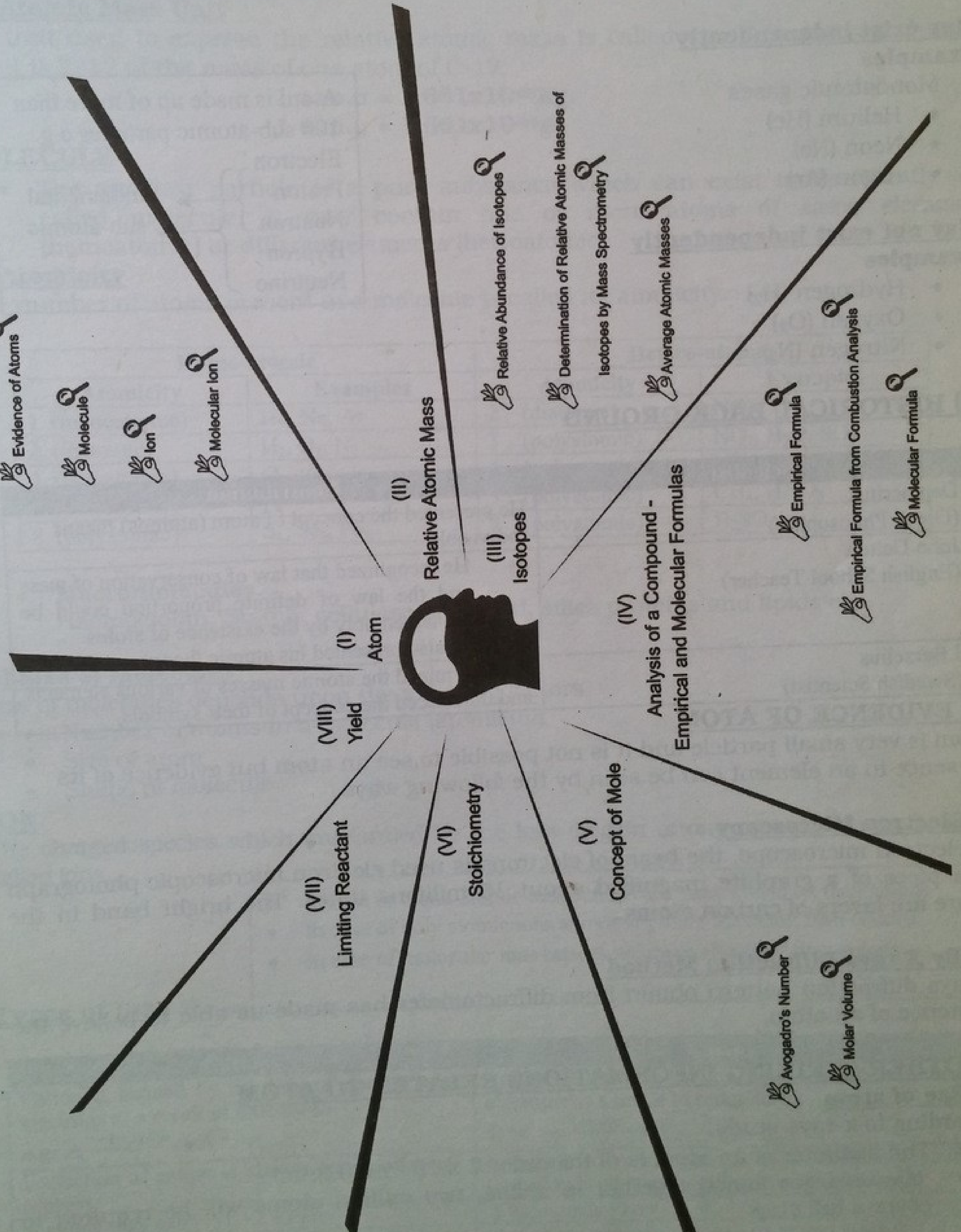
KIPS ENTRY TEST SERIES

Part - I

KIPS PUBLICATION

Chapter 1

BASIC CONCEPTS


(I) Atom
Evidence of Atoms
Molecule
Ion
Molecular Ion
(II) Relative Atomic Mass
Relative Abundance of Isotopes
Determination of Relative Atomic Masses of Isotopes by Mass Spectrometry
Average Atomic Masses
(III) Isotopes
(IV) Analysis of a Compound - Empirical and Molecular Formulas
Empirical Formula
Empirical Formula from Combustion Analysis
Molecular Formula
(V) Concept of Mole
Avogadro's Number
Molar Volume
(VI) Stoichiometry
(VII) Limiting Reactant
(VIII) Yield

Chapter 1

Basic Concepts

ATOM

The smallest particle of an element which may or may not have an independent existence is called an atom.

Atom is made up of more than 100 sub-atomic particles e.g.
Electron
Proton
Neutron
Hypron
Neutrino
→ fundamental
→ sub-atomic

May exist independently

Examples

Monoatomic gases

- Helium (He)
- Neon (Ne)
- Argon (Ar)

May not exist independently

Examples

- Hydrogen (H_2)
- Oxygen (O_2)
- Nitrogen (N_2)

(a) HISTORICAL BACK GROUND

Scientist	Contribution
Democritus (Greek Philosopher)	He presented the concept of atom (atomos) means indivisible.
John Dalton (English School Teacher)	1- He recognized that law of conservation of mass and the law of definite proportion could be explained only by the existence of atoms. 2- He also presented his atomic theory
J.Berzelius (Swedish Scientist)	He determined the atomic masses of various elements and introduced the concept of their symbols

(b) EVIDENCE OF ATOM

Atom is very small particle and it is not possible to see an atom but evidence of its presence in an element can be seen by the following ways.

(i) Electron Microscopy

In electron microscope, the beam of electrons is used electron microscopic photograph of a piece of a graphite magnified about 15 millions times. The bright band in the figure are layers of carbon atoms.

(ii) By X-rays Diffraction Method

X-rays diffraction pattern obtain from diffractometer has made us able to believe the existence of an atom.

(c) OTHER STRIKING INFORMATIONS RELATED TO ATOM

(i) Size of atom

According to x-rays study.

- The diameter of an atom is of the order 2×10^{-10}m (0.2nm)
- If atoms are joined together in a line, two million atoms will be required to cover a full stop.

(ii) Mass of an atom

The mass of an atom ranges from $10^{-27} - 10^{-25}$kg or $10^{-24} - 10^{-22}$g).

(iii) Atomic Mass Unit

The unit used to express the relative atomic mass is called atomic mass unit (amu) and it is 1/12 of the mass of one atom of C-12.

1 a.m.u = 1.661×10^{-27}kg.
1 a.m.u = 1.661×10^{-24}g.

MOLECULE

- The smallest particle of a pure substance which can exist independently is called molecule. It may contain one or more atoms of same element (homoatomic) or different elements (hetroatomic).

(a) Atomicity

The number of atoms present in a molecule is called its atomicity.

Homo-atomic		Hetero-atomic	
Atomicity	Examples	Atomicity	Examples
1 (monoatomic)	He, Ne, Ar	2 (diatomic)	NO, CO
2 (diatomic)	H_2, O_2, N_2	3 (polyatomic)	NO_2, H_2O, SO_2
3 (polyatomic)	O_3	4 (polyatomic)	NH_3, SO_3, H_2O_2
4 (polyatomic)	P_4	5 (polyatomic)	CH_4, HNO_3
8 (polyatomic)	S_8, Se_8, Po_8	7 (polyatomic)	H_2SO_4

- **Macromolecules**
  Haemoglobin, Starch, cellulose, diamond, silica proteins and lipids etc.

(c) Size of molecules

Size of molecules depends upon the following factors

- Number of atoms in a molecule (atomicity)
- Size of atom
- Shape of molecule

ION

The charged species which are formed by the loss or gain of one or more electrons are called ions.

- In case of mono-atomic ions cations are more abundant than anions
- In case of poly atomic ions anions are more abundant than cations.
- In case of molecular ions cations are more abundant than anions.

Types of Ions

Cations	Anions
Cation is formed by the loss of one or more electrons as a result of oxidations. e.g. $A \xrightarrow{\text{oxidation}} A^{\oplus} + e^-$	Anions is formed by the gain of one or more electrons as a result of reduction. $B + e^- \xrightarrow{\text{reduction}} B^-$
Formation of cation is always an endothermic process.	Formation of uni-negative ion is exothermic but formation of all other negative ions is endothermic.
A cation may carry +1,+2,+3 etc.	A anion may carry –1,-2,-3 etc.
Size of cation is smaller than its parent atom.	Size of anion is greater than its parent atom.

MOLECULAR ION

The charged molecular species formed by the loss or gain of electron are called molecular ions.

Types of molecular ion

(a) Cationic molecular ion $(CH_4^{\oplus}, CO^{\oplus}, N_2^{\oplus})$

(b) Anionic molecular ion $(C(CH_3)_4\ C^{-})$

POINT TO BE REMEMBERED

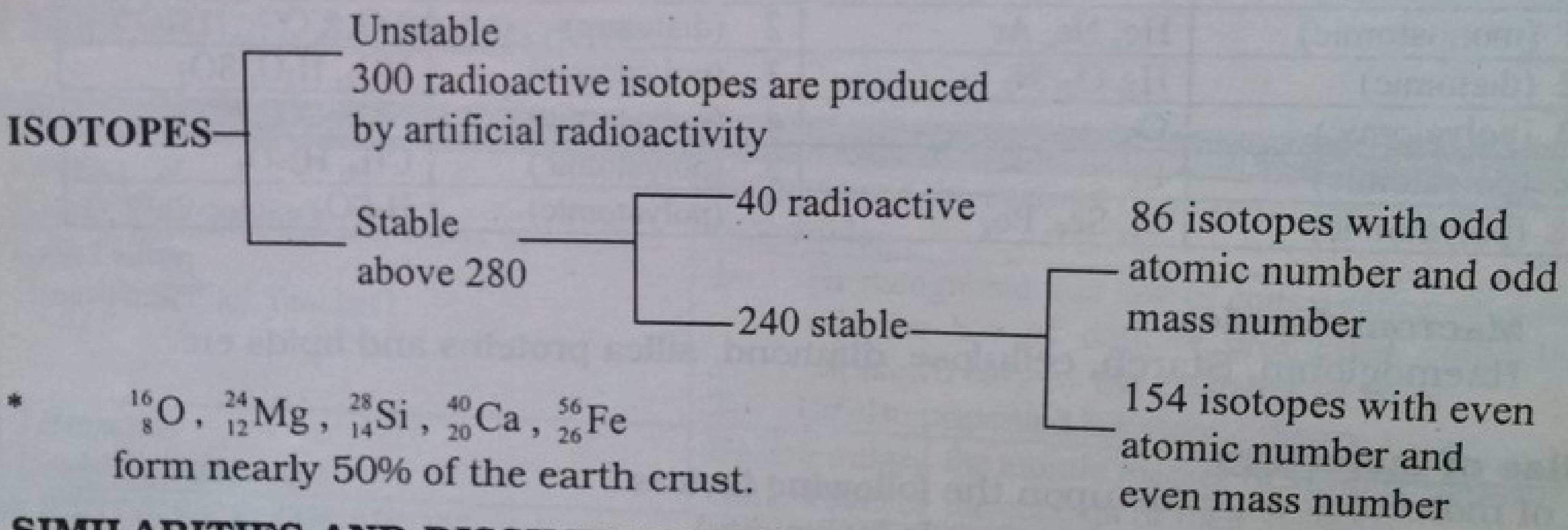
- Number of cationic molecular ions is greater than the number of anionic molecular ions.

ISOTOPES

Atoms of the same element having different mass number are called isotopes. The concept of isotopy was introduced by Soddy.

Occurrence

Elements occur in the nature in the form of isotopes. Occurrence of isotopes has been shown here.


ISOTOPES
Unstable
300 radioactive isotopes are produced by artificial radioactivity
Stable above 280
40 radioactive
240 stable
86 isotopes with odd atomic number and odd mass number
154 isotopes with even atomic number and even mass number

* $^{16}_{8}O$, $^{24}_{12}Mg$, $^{28}_{14}Si$, $^{40}_{20}Ca$, $^{56}_{26}Fe$ form nearly 50% of the earth crust.

SIMILARITIES AND DISSIMILARITIES IN ISOTOPES OF ELEMENTS

Similarities	Dissimilarities
Same, • Atomic number • Number of Protons • Electronic configuration • Position in periodic table • Chemical properties	Different, • Mass number • Number of Neutrons • Physical properties • Half life • Rate of reaction

CLASSIFICATION OF ELEMENTS ON THE BASIS OF ISOTOPES

- Mono-isotopic elements (F, I, As, Au)
- Di-isotopic elements (Cl, Br)
- Tri-isotopic elements (H_2, O_2, N_2)
- Tetra-isotopic elements (S)
- Penta-isotopic elements (Ni)
- Hexa-isotopic elements (Ca, Pd)
- Nano-isotopic elements (Cd)
- Undeca-isotopic elements (Sn)

TERMINOLOGY RELATED TO ISOTOPES

1- Mass number
2- Relative abundance

MASS SPECTROMETER

An instrument which is used to measure the exact masses of different isotopes of an element together with their relative abundances is called mass spectrometer.

Types of mass spectrometer

- Aston's mass spectrometer
  It was designed to identify isotopes of an element on the basis of atomic masses.
- Dempster's mass spectrometer
  It was designed to identify isotopes of an element which are in the solid state. It has five parts.

Parts of Spectroscope

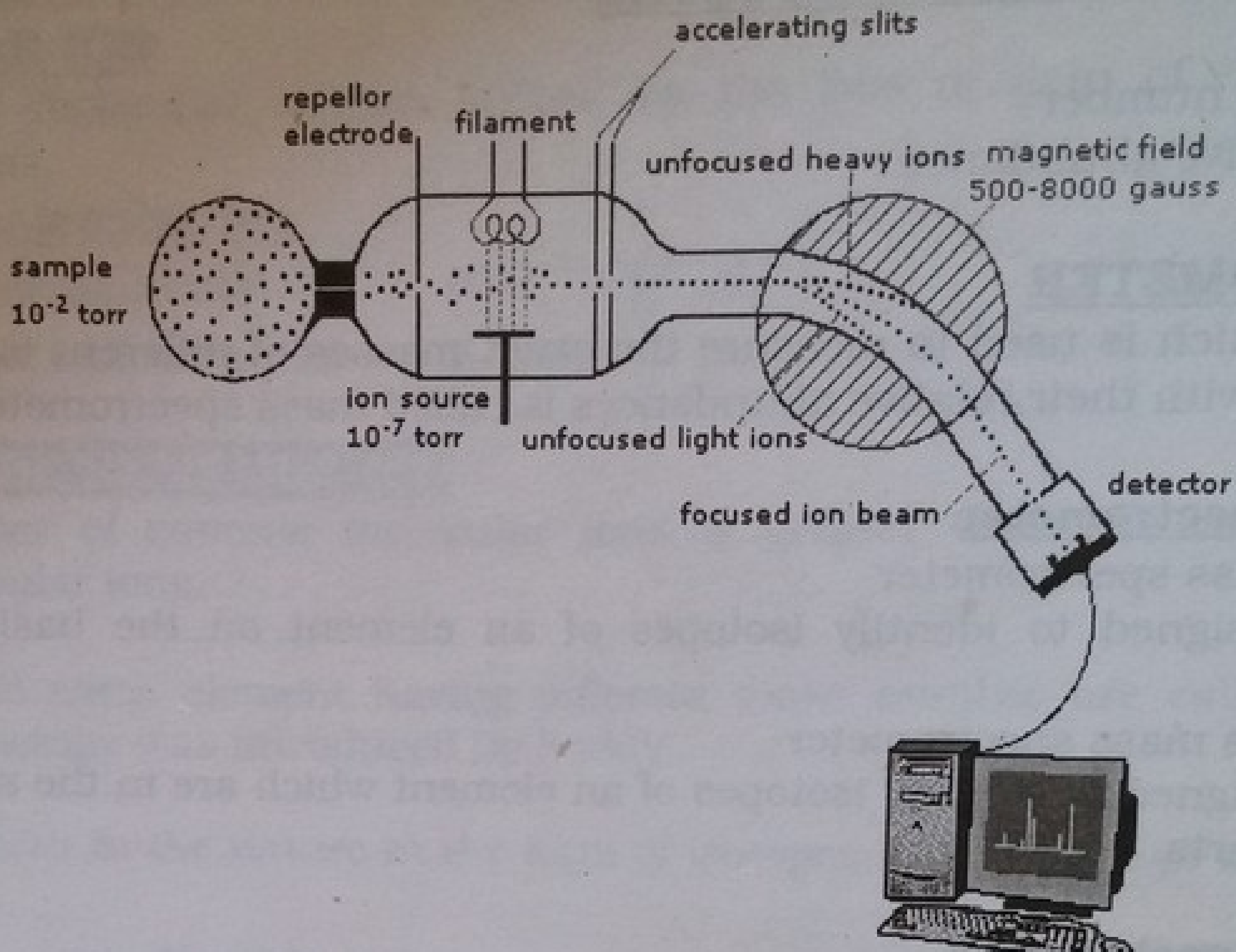
- Vaporization chamber
- Ionization chamber
- Electric field
- Magnetic field
- Ion collecter
- Recorder
- Amplifier

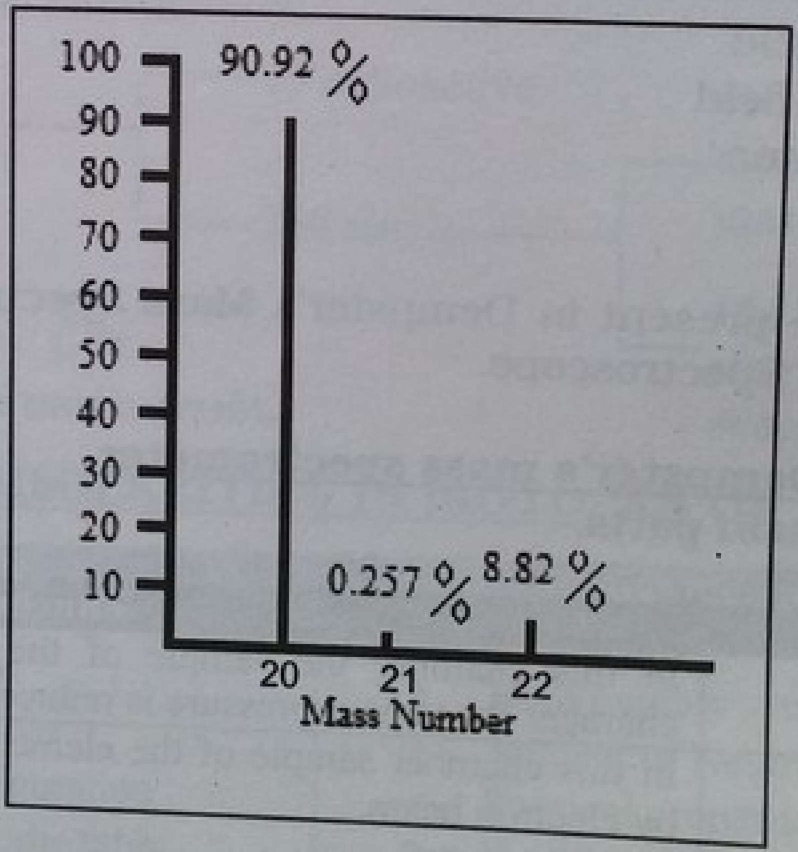
The first five parts are present in Dempster's Mass Spectrometer while last two parts are present in Modern Spectroscope.

Instrumentation of Dempster's mass spectrometer

It has following five main parts.

Stages	Function
Vapourization chamber	In this chamber the sample of the element is vapourized. In this chamber the vapour pressure is reduced to 10^{-7}-10^{-6}torr
Ionization chamber	In this chamber sample of the element is ionized either by α -rays or by electron beam. $e^- + X \rightarrow X^{\oplus} + e^- + e^-$
Electric field	Electric field is applied to accelerate the positive ions. The applied potential difference is of 500-2000 volts.
Magnetic field	On passing through magnetic field, deflection of positive ions takes place according to their mass/charge ratio. $\frac{m}{e} = \frac{H^2 r}{E}$
Electrometer or ion collector	Ion collector receives positive ions according to their mass/charge ratio related to isotopes. 1- The strength of current measured by ion collector gives the relative abundance of ions of a definite m/e value. 2- The same experiment is performed with C-12 isotopes and the current strength is compared.





Computer plotted graph for the isotopes of Neon (Ne)

OTHER TECHNIQUES FOR THE SEPARATION OF ISOTOPES

- Gaseous diffusion
- Thermal diffusion
- Distillation
- Ultra centrifuge
- Electromagnetic separation
- Laser separation

RELATIVE ATOMIC MASS

Relative atomic mass is the mass of an atom of an element as compared to the mass of an atom of carbon taken as 12.

Chlorine

Isotopes	${}^{35}_{17}Cl$	${}^{37}_{17}Cl$
Relative abundance	75%	25%

$$\text{Relative atomic mass of Cl} = \frac{35 \times 75 + 37 \times 25}{100}$$

$$\text{Relative atomic mass} = 26.25 + 9.25 = 35.5 \text{ amu}$$

Neon

Isotopes	${}^{20}_{10}Ne$	${}^{21}_{10}Ne$	${}^{22}_{10}Ne$
Relative abundance	90.92%	0.26%	8.82%

$$\text{Relative atomic mass of Neon} = \frac{20x90.92+21x0.26+22x8.82}{100} = 20.18 \text{ amu}$$

ANALYSIS OF A COMPOUND

Qualitative analysis

Identification of types of elements present in a compound present in a compound.

Quantitative analysis

Determination of ratio between the masses of all the elements.

METHODS TO DETERMINE PERCENTAGE COMPOSITION

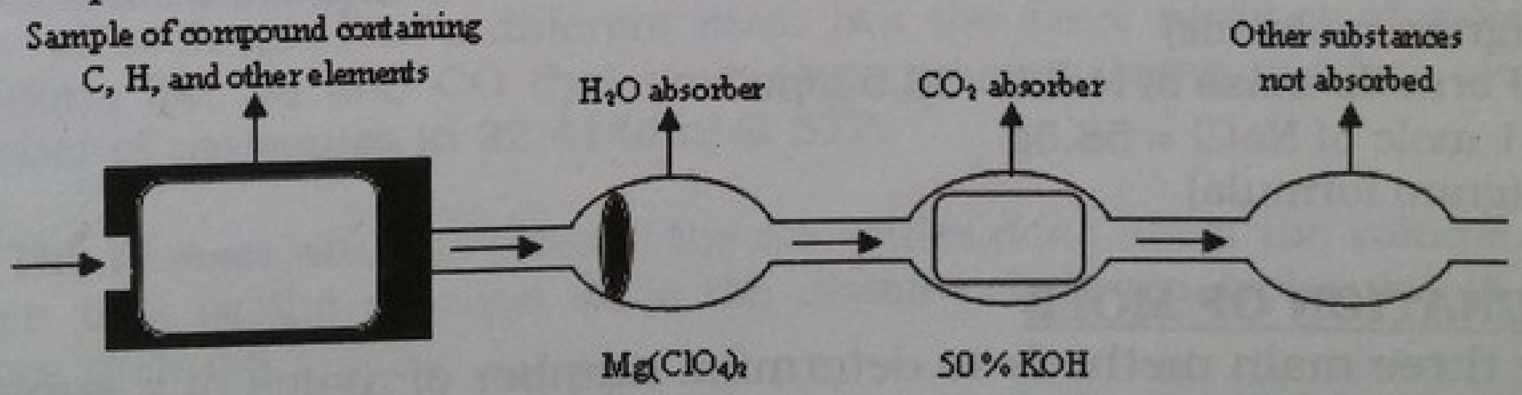
(a) Percentage composition

The percentage composition obtained from a given formula of a compound is called theoretical percentage composition.

$$\%\text{age of an element} = \frac{\text{Number of atoms x at.mass of element}}{\text{molecular formula of the compound}} \times 100$$

(b) Combustion analysis

The sequence of combustion analysis is shown in the following diagram.



- By combustion analysis only those organic compounds can be analyzed which simply contain carbon, hydrogen and oxygen.
- From the masses, percentages are calculated by using the following formulae:-

(a) $$\%\text{age of carbon} = \frac{\text{mass of } CO_2 \text{ obtained in experiment}}{\text{mass of organic compound}} \times \frac{12.01}{44.01} \times 100$$

(b) $$\%\text{age of hydrogen} = \frac{\text{mass of } H_2O \text{ obtained in experiment}}{\text{mass of organic compound}} \times \frac{2.0}{18.0} \times 100$$

(c) %age of oxygen = 100 – (% of carbon + % of Hydrogen)

DIFFERENCE BETWEEN EMPIRICAL AND MOLECUALR FORMULA

Empirical formula	Molecular formula
A formula which represents the simple whole number ratio of atoms of elements in a compound is called empirical formula.	A formula which represents actual number of atoms of each elements in a molecular compound is called molecular formula.
It is obtained from %age composition of elements i.e. chemical analysis	It is obtained by multiplying 'n' with empirical formula
This term is used for both molecular and ionic compounds	This term is used only for molecular compounds
Examples: NaCl, CH_2O, CH are empirical formulae of sodium chloride, glucose and benzene respectively.	Examples: $C_6H_{12}O_6$ & C_6H_6 are molecular formulae of glucose and benzene respectively.

Note:-
The term empirical formula is used for ionic compounds and giant covalent structures (sand SiO_2, graphite & diamond C). It is also used for covalent compounds as CH_2O for glucose and acetic acid.

RELATIONSHIP BETWEEN EMPIRICIAL AND MOLECUALR FORMULA

Molecular formula = n × empirical formula

MOLE

The atomic mass of an element, relative molecular mass of covalent compound or formula mass of ionic compound expressed in grams is called mole.

Examples

(i) Atomic mass of Na = 23.0 amu
1 mole of Na = 23.0g
(gram atom of Na)

(ii) Molecular mass of H_2O = 18.0 amu
1 mole of H_2O = 18.0g
(gram molecule)

(iii) Formula mass of NaCl = 58.5 amu
1 mole of NaCl = 58.5g
(gram formula)

DETERMINATION OF MOLE

There are three main methods to determine number of moles of a substance.

1- When mass of substance is given in grams.

$$\text{No of moles of substance} = \frac{\text{mass in grams of given substance}}{\text{atomic mass/molecular mass/formula mass}}$$

2- For a certain number of particles (atoms, ions or molecules)

$$\text{Number of moles of a substance} = \frac{\text{Number of particles of given substance}}{6.022\times10^{23}}$$

3- For volume of a given gas in dm^3 at STP.

$$\text{Number of moles of gas} = \frac{\text{Volume of gas in } dm^3 \text{ at STP}}{22.4\times dm^3}$$

One mole	**Particles**	6.022×10^{23} Atoms	6.022×10^{23} Molecules	6.022×10^{23} Formula Units	6.022×10^{23} Ions
	Mass	Gram Atomic Mass of Element	Gram molecular Mass of substance	Gram Formula Mass of formula unit	Gram Ionic Mass of ion
	Volume	At S.T.P (of gas) = $22.4\ dm^3$			

AVOGADRO'S NUMBER

It is the number of particles (atoms, ions or molecules) present in one mole of a substance. It is denoted by N_A. Its value is 6.022×10^{23}.

Examples

(i) Atomic mass of Na = 23.0 amu
1 mole (23.0g) of Na = 6.022×10^{23} atoms

(ii) Molecular mass of H_2O = 18.0 amu
1 mole (18.0g) of H_2O = 6.022×10^{23} molecules

(iii) Formula mass of NaCl = 58.5 amu
1 mole (58.5g) of NaCl = 6.022×10^{23} formula units

MOLAR VOLUME

One mole of an ideal gas at standard temperature and pressure (STP) occupies a volume of $22.414 dm^3$. This volume of $22.414 dm^3$ is called molar volume and its true only when the gas is ideal. With the help of this information, we can convert the mass of a gas at STP into its volume and vice versa.

Hence we can say that

(i) 2.016g of H_2 = 1 mole of H_2 = 6.02×10^{23} molecules of H_2 = $22.414 dm^3$ of H_2 at STP.

(ii) 16g of CH_4 = 6.02×10^{23} molecules of CH_4 = $22.414 dm^3$ of CH_4 at STP.

Point to be remembered: - It is very interesting to know from the above data that $22.414 dm^3$ of each gas has a different mass but the same number of molecules with few exceptions like N_2 and CO that have same masses, same number of atoms and same number of molecules in $22.414 dm^3$ at STP.

Reason:- The masses and the sizes of the molecules don't affect the volume. Normally, it is known that in the gaseous state the distance between molecules is 300 times greater than their diameters.

STOICHIOMETRY

Stoichiometry is a branch of chemistry, which tells us the quantitative relationship between reactants and products in a balanced chemical equation.

LIMITATION OF CHEMICAL EQUATIONS

They do not tell about the

(i) Conditions (Temperature and pressure)
(ii) Rate of reaction
(iii) Physical state of reactants and products.
(iv) Mechanism of reaction

CONDITIONS FOR STOICHIOMETRIC CALCULATIONS

Stoichiometeric calculations are based on the following conditions:-

1- All the reactants must be completely converted into the products.
2- The side reaction must not occur.
3- The law of conservation of mass and the law of definite proportions must be obeyed while doing the calculations.

The following types of relationship can be studied with the help of a balanced chemical equation.

$2H_{2(g)}$	+	$O_{2(g)}$	$\longrightarrow$	$2H_2O_{(g)}$	$\Delta H = -482\ kJ/mol$
2-moles		1-mole		2-moles	
4g		32g		36g	
$44.828dm^3$		$22.414dm^3$		$44.828dm^3$	

(1) Mass-mass Relationship

If we are given the mass of one substance, we can calculate the mass of the other substance.

(2) Mass-mole Relationship or Mole-mass Relationship

If we are given the mass of one substance, we can calculate the moles of other substance and vice versa.

(3) Mass-volume Relationship

If we are given the mass of one substance, we can calculate the volume of the other substances and vice versa.

(4) Mole-mole Relationship

If we are given the mole of one substance, we can calculate the mole of the other substances and vice versa.

LIMITING REACTANT

Limiting reactant is a reactant that controls the amount of the products formed in a chemical reaction due to being less than the required amount. It can also be defined as follow: -

1- It is a reactant that produces least number of moles of product.
2- It is consumed earlier in the reaction.

Identification of Limiting Reactant

To identify a limiting reactant, the following three steps are performed.

1- Calculate the number of moles from the given amount of reactants.
2- Calculate the number of moles of product formed from the given moles of each reactant.
3- Identify the reactant as limiting reactant which produces least moles of product.

YIELD

The amount of the product obtained as a result of the chemical reaction is called yield.

Types of Yield

(a) Theoretical Yield

The amount of the product calculated from the balanced chemical equation is called the theoretical yield.

(b) Actual Yield

The amount of the product obtained in a chemical reaction experimentally is called actual yield.

(c) Percentage Yield

$$\% \text{ yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

Point to be remembered: - Actual yield is always less than theoretical yield.

Reasons:-

(i) A practically inexperienced worker has many shortcomings and cannot get the expected yield.

(ii) The processes like filtration crystallization if not properly carried out, decrease the theoretical yield.

(iii) Some of the reactants might take part in a competing side reaction and reduce the amount of the desired product.

PRACTICE EXERCISE

30 mins
Time Yourself

1. Diameter of an atom is in the order of
   (a) 0.2m (b) 0.2mm
   (c) 0.2nm (d) 0.2pm
2. Which of the following are isoelectronic species?
   (a) H^+, H, H^- (b) Li^+, Na^+, K^+
   (c) Cl^-, Br^-, I^- (d) F^-, Ne, Na^+
3. Mass spectrometer is used to determine Mass number of isotopes and
   (a) Atomic number (b) Relative abundance
   (c) Electronic configuration (d) All of the above
4. Molecular ions are formed by passing
   (a) High energy electron beam (b) α -particle
   (c) X-rays (d) all of the above
5. The number of peaks obtained in mass spectrometry shows
   (a) Relative abundance (b) Average mass of element
   (d) Number of isotopes (d) Relative isotopic mass
6. Empirical formula of chloroform is
   (a) CH_2Cl_2 (b) CH_3Cl
   (c) CCl_4 (d) $CHCl_3$
7. Which one is true about isotope?
   (a) Same number of neutrons (b) Same mass number
   (c) Same physical properties (d) Same chemical properties
8. Molecular mass of water (18g) means
   (a) 1-mole molecules of water (b) 1-gram molecule of water
   (c) 3-gram atoms (d) All
9. Which of the following ion formation is always exothermic?
   (a) Uni-negative (b) Uni-positive
   (c) Di-negative (d) Di-positive
10. Which of the following statements about isotopes is correct?
    (a) Isotopes with odd atomic number are abundant
    (b) Isotopes with odd atomic number and even mass number are abundant
    (c) Isotopes with even atomic number and even mass number are abundant
    (d) Isotopes with even atomic number and odd mass no are abundant
11. The sample of isotopes of an element which needs not to be vaporized in the vaporization chamber
    (a) Gas
    (c) Volatile solid (b) Liquid
    (d) All
12. One mole of CO_2 contains.
    (a) $6.022x10^{23}$ atoms of oxygen (b) 22-gram electrons
    (c) $6.022x10^{23}$ atoms of carbon (d) both b & c

13. Avogadro's number may represent.
(a) volume of particles (b) number of particles
(c) mass of particles (d) all of the above

14. The number of isotopes of elements with even mass number and even atomic number are.
(a) 280 (b) 300
(c) 154 (d) 54

15. Size of molecule depends upon
(a) Atomicity (b) Shape of molecule
(c) Both a and b (d) Difficult to predict

16. Which of the following terms is not used for ionic compound?
(a) formula unit (b) empirical formula
(c) molecular formula (d) formula mass

17. 0.36 moles of each aluminium and oxygen react with each other to produce aluminium oxide. The amount of product formed is
(a) 0.18mole (b) 0.27mole
(c) 0.24mole (d) 0.09mole

18. Which of the following terms is used for the mass of chlorine 35.5?
(a) relative atomic mass (b) mass number
(c) atomic weight (d) relative isotopic mass

19. Which one of the following has the maximum number of isotopes?
(a) oxygen (b) carbon
(c) tin (d) chlorine

20. Which one of the following is not the mono isotopic element?
(a) arsenic (b) uranium
(c) iodine (d) nickel

21. The volume occupied by 2.8 g of N_2 at STP
(a) 2.24 dm^3 (b) 22.4 dm^3
(c) 1.12 dm^3 (d) 112 cm^3

22. The mass of decimole of electrons (N_A) is
(a) 1.008 mg (b) 0.184 mg
(c) 0.054 mg (d) 5.4 mg

23. The number of moles of CO_2 which contains 16 g of oxygen is
(a) 0.25 (b) 0.50
(c) 0.75 (d) 1.00

24. Which of the following statements is wrong about isotopes?
(a) they possess different mass number
(b) they possess different physical properties
(c) they possess same chemical properties
(d) they possess different position in the periodic table

25. How many isotopes have odd atomic number?
(a) 154 (b) 280
(c) 86 (d) 300

26. Qualitative analysis is carried out for
(a) identification of elements (b) estimation of amounts of elements
(c) molar ratio of elements (d) molar volume of elements

27. Percentage of calcium in calcium carbonate is
(a) 80% (b) 30%
(c) 40% (d) 20%

28. Combustion analysis is performed to determine
(a) Empirical formula (b) Molecular mass
(c) Molecular formula (d) Formula mass

29. Mostly elements have fractional atomic masses because of
(a) mass of an atom itself is in fraction
(b) atomic masses are average masses of isobars
(c) atomic masses are average masses of isotopes proportional to their relative abundance
(d) atomic masses are average masses of isotopes

30. Isotopes differ in
(a) properties which depend upon mass
(b) arrangement of electrons in orbitals
(c) chemical properties
(d) all of the above

31. Which of the following is not a macromolecule?
(a) sand (b) haemoglobin
(c) diamond (d) maltose

32. Which of the following methods is used to estimate hydrogen in an organic compound?
(a) Combustion method (b) Duma's method
(c) Kjeldahl's method (d) All of the above methods are for different purposes

33. Isotopes of the same elements has
(a) different number of protons
(b) same number of neutrons
(c) different number of neutrons
(d) same mass number (nucleon number)

34. The nucleus of an atom of every element will always contain
(a) neutrons
(b) protons and electrons
(c) protons
(d) protons and neutrons

35. When cationic molecular ions are allowed to pass through strong magnetic field in mass spectrometer, which of the following ions is fallen first?
(a) lighter (b) intermediate
(c) heavier (d) are collected at same time

36. When 0.5 mole of phosphoric acid is dissolved in aqueous solution, how many moles of –ve and +ve ions are collected altogether?
(a) 0.5 (b) 1.0
(c) 1.5 (d) 2.0

37. For which of the following compounds the term empirical formula cannot be applied?
(a) NaCl (b) H_2O
(c) CCl_4 (d) It can be applied to all mentioned above

38. Dempsters mass spectrometer has number of zones/parts
(a) 5 (b) 4
(c) 3 (d) 2

39. The properties of an element mostly corresponds to that isotope which has greater

(a) Mass number (b) Atomic mass

(c) Relative abundance (d) All of the above

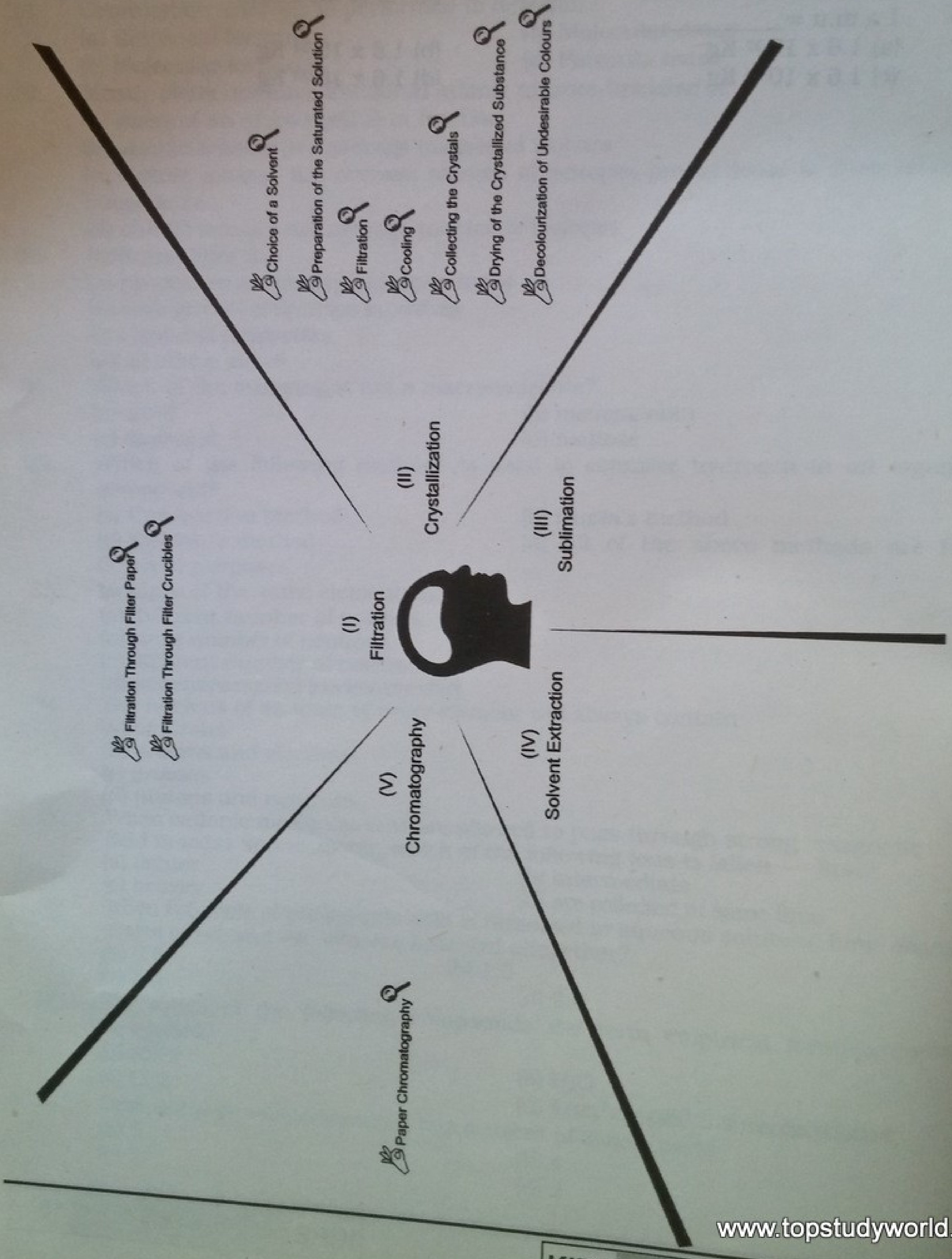
40. 1 a.m.u = ___________

(a) 1.6×10^{-27} Kg (b) 1.6×10^{-24} Kg

(c) 1.6×10^{-26} Kg (d) 1.6×10^{-28} Kg

Chapter 2

EXPERIMENTAL TECHNIQUES IN CHEMISTRY


(I) Filtration
Filtration Through Filter Paper
Filtration Through Filter Crucibles
(II) Crystallization
Choice of a Solvent
Preparation of the Saturated Solution
Filtration
Cooling
Collecting the Crystals
Drying of the Crystallized Substance
Decolourization of Undesirable Colours
(III) Sublimation
(IV) Solvent Extraction
(V) Chromatography
Paper Chromatography

Chapter 2

Experimental Techniques In Chemistry

ANALYTICAL CHEMISTRY

The branch of chemistry which gives a complete chemical characterization (both qualitative and quantitative analysis) of a compound is called analytical chemistry.

QUALITATIVE ANALYSIS

The analysis in which the detection or identification of the elements present in a compound is carried out is called qualitative analysis.

Examples

(i) Salt analysis
(ii) Detection of functional groups

QUANTITATIVE ANALYSIS

The analysis in which relative amounts of the elements are determined is called quantitative analysis.

Example:-
Volumetric analysis.

STEPS FOR QUANTITATIVE ANALYSIS

(i) Obtaining a sample for analysis.
(ii) Separation of desired constituents.
(iii) Measurement and calculation of results.
(iv) Drawing conclusion from the analysis.

Method of purification	Application
Filtration	Separation of soluble and insoluble solids
Evaporation	Separation of a soluble solid from the solution
Crystallization	Separation of a solid by cooling either its solution or molten liquid
Decanting and Centrifuging	Separation of suspension
Simple distillation	Separation of a liquid from a solution
Fractional distillation	Separation of a fraction from a mixture of miscible liquids
Separating funnel	Solvent extraction from the solution.
Sublimation	Separation of sublimant from mixture of solids
Chromatography	Separating colours, dyes, amino acid, etc

FILTRATION

This process is used to separate insoluble particles from liquids and it can be performed with several types of filter media.

METHODS OF FILTRATION

(i) Filtration through filter paper
    (a) Ordinary filter paper
    (b) Fluted filter paper
(ii) Filtration through filter crucibles
    (a) Gooch crucible
    (b) Sintered glass crucible

Filtration through filter paper Slow process	Filtration through crucible Fast process
▪ Solvent passes through filter paper and insoluble particles remains on filter paper. ▪ Filter papers are classified on their size of pores. ▪ Filter paper should be filled with ppt. upto 1/4 -1/2. ▪ Tip of stem should be in touch of beaker to avoid any splashing. ▪ Fluted filter paper is obtained by folding normal filter paper in such a way that a fan like with alternate elevations and depressions is obtained.	Two types of crucibles are available 1. Gooch crucible ▪ Made up of porcelain clay ▪ Perforated bottom is covered by paper pulp or filter paper ▪ Used for filtration of those ppts. which need to be ignited at high temperature. ▪ Asbestos is used instead of filter paper for those chemicals, which have a reaction with paper. 2. Sintered glass crucible ▪ Made up of glass ▪ Porous glass disc in bottom act as sieve. (filter medium)

DIFFERENCE BETWEEN GOOCH AND SINTERED GLASS CRUCIBLE

Gooch Crucible	Sintered Glass Crucible
• It is made up of porcelain.	• It is made up of glass.
• It has a porous base.	• In its base sintered glass disc is sealed.
• Its base needs to be covered with a filter paper or an asbestos mat.	• There is no need to cover the base with filter paper or asbestos mat.
• Reactive solutions like HCl, $KMnO_4$ can not be filtered if base is covered with filter paper.	• Reactive solutions can safely be filtered.
• To filter the reactive solutions, base is covered with asbestos mat.	• There is no need of any alteration.
• There is contamination of filter paper with the crystals.	• There is no contamination.

CRYSTALLIZATION

Separation of solid as crystals when hot saturated solution is cooled is called crystallization.

Choice of solvent

- Solvent is selected by hit and trial method.
- Suitable solvent dissolves excess of solute at high temperature and less amount of solute at room temperature.
- Solvent should not react with solute.
- Impurities should not be dissolved in solvent, if they get dissolved then should not be separated out as crystals along with solute.
- On cooling, it should deposit well formed crystals of pure compound.
- It should be cheaper.
- It should be safe and should be easily removable.

Solvents for Crystallization

Mostly used solvents are water, rectified spirit, ethanol, diethyl ether, acetone etc.

NOTE:-

If single solvent is not found suitable then combination of two or more solvents can be employed.

Precaution

If solvent is inflammable then water bath is used for heating purposes so that it does not catch the fire.

PREPARATION OF SATURATED SOLUTION

The solute is dissolved in minimum amount of solvent at its boiling point to form a saturated solution.

Filtration

- Fluted filter paper or normal filter paper is used for the filtration of a hot solution.
- The filtration of a hot solution avoids premature crystals

Cooling

- Solution is cooled down at moderate rate crystals of pure compound will be produced.

Collection of crystals

- Gooch crucible is used for the separation of crystal.

Drying of crystallized substances

- Drying can be done by placing the crystals between the folds of filter paper.
- Drying can be done by heating the crystals in oven.
- Vacuum desiccators are used to dry the crystals
- $CaCl_2$, P_2O_5 and Silica gel are used in dessicator to absorb moisture.

Decolorization of undesirable colours.

- Crystals with deposition of coloring matter or resinous products are dissolved in solvent and boiled
- Solvent contains animal charcoal, which will adsorb colour.
- The solution is filtered in hot state.
- Moderate cooling is carried out.
- Crystals of pure substance will be separated out.

SUBLIMAITON

The process in which, solid when heated, vapourizes directly without passing through the liquid phase is called sublimation.

Examples

(i) naphthalene (ii) iodine (iii) ammonium chloride (iv) benzoic acid (v) camphor (vi) anthracene (vii) anthraquinone (viii) hexachloroethane

SOLVENT EXTRACTION

Solvent extraction technique involves the separation of a solute from a solution by shaking the solution with an immiscible solvent in which the solute is more soluble. This technique is mostly applied to separate organic compounds from water.

Distribution Law or Partition Law

I. A solute distributes itself between two immiscible liquids in a constant ratio of concentrations irrespective of the amount of solute added.

Steps for Solvent Extraction

(i) Take a solution containing solute e.g. (I_2 dissolved in H_2O+KI system in the form of I_3^-) in a separating funnel.

(ii) Add small amount of an immiscible solvent (e.g. CCl_4) in the separating funnel

(iii) Shake them well.

(iv) Separate the CCl_4 layer

(v) Evaporate the organic solvent to get dried crystals.

Repeat steps (ii) to (v) again and again for better extraction.

CHROMATOGRAPHY

The word chromatography originates from the Greek word "Khromatos" meaning colour writing.

A technique used for the separation of components of a mixture which involves the distribution of a solute between stationary phase and mobile phase is based on partition law or distribution law.

Stationary Phase

- It may be solid or liquid
- It may be packed in a column
- It may be spreaded as a layer or distributed as a film
- Examples:- Silica gel, alumina etc.

Mobile Phase

- It is also called eluent
- It competes with stationary phase for components of the mixture
- Examples:- Water, ethanol, acetic acid, acetone or a gas etc.

Principle of chromatography

The principle involved in chromatography depends upon the relative solubilities of the components between two phases. It is governed by distribution coefficient (K_d).

Classification of Chromatography

It can be classified in three ways:-

1- On the basis of shape
2- On the basis of phase
3- On the basis of mechanism

The Russian Botanist Mikhail Tswett was the first to understand the basis of chromatography and to apply it systematically as a method of separation.

Difference between adsorption and partition chromatography

Adsorption Chromatography	Partition Chromatography
1. The type of chromatography in which physical forces are involved in retentive ability of solute particles with stationary phase is called adsorption chromatography. 2. In adsorption chromatography, a solid is used as stationary phase. 3. Examples-	1. The type of chromatography in which separation involves distribution of the components is called partition chromatography. 2. In partition chromatography, liquid [illegible] liquid supported [illegible]

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2. In adsorption chromatography, a solid is used as stationary phase.	2. In partition chromatography, liquid or liquid supported on solid act as stationary phase.
3. Examples:- Column chromatography, thin layer chromatography (TLC).	3. Example:- Paper chromatography.

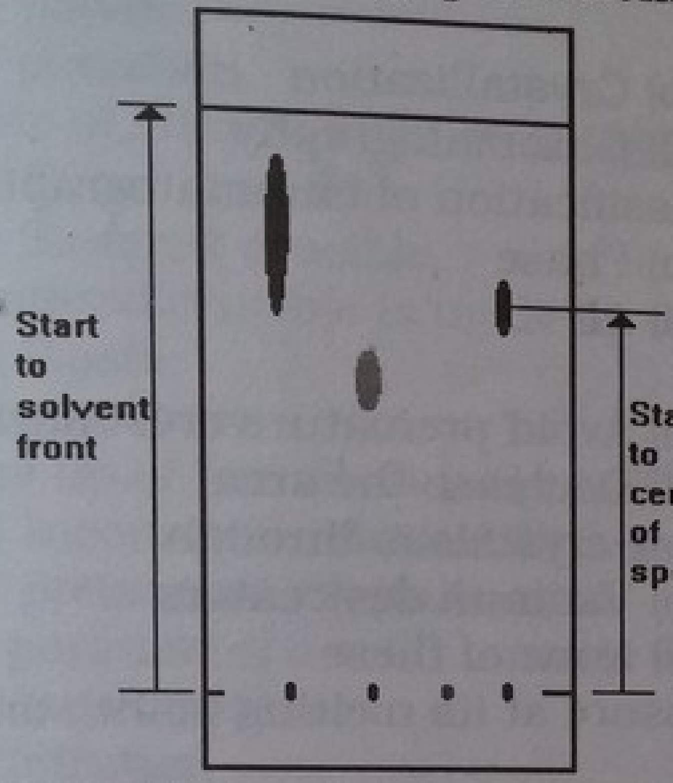
Paper Chromatography

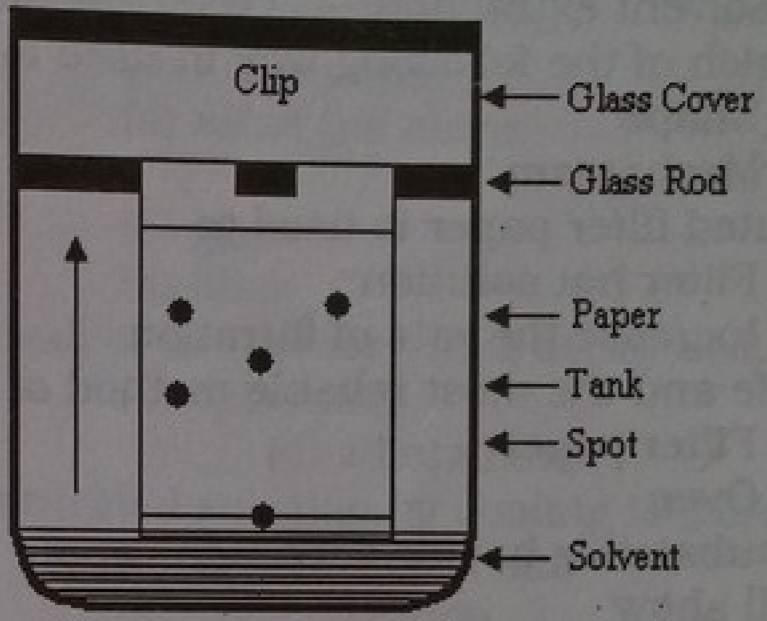
In 1944, Consden Gordon and Martin introduced paper chromatography.

Different ways of paper chromatography

There are three common ways of carrying out this technique:-

1- Ascending paper chromatography (solvent rises up)
2- Descending paper chromatography (solvent flows down)
3- Radial/circular paper chromatography (solvent flows in circular fashion)





Uses of Chromatography

1- Separation and identification of coloured pigments.
2- Identification of medicines and proteins.
3- Analysis of urine.
4- Determination of purity of compounds.
5- Used in organic synthesis for separation, isolation and purification of the products.
6- Equally important in qualitative and quantitative analysis.

IMPORTANT DEFINITIONS AND TERMINOLOGIES

Soluble	A substance that is dissolved.
Insoluble	A substance that is not dissolved.
Solute	Normally a solid, which gets dissolves.
Solvent	Normally a liquid which dissolves solute
Solution	Solute + solvent (Homogeneous mixtures)
Residue	Insoluble solid which is left over the filter media.
Filtrate	A solution that passes through the filter paper.
Crystal	A solid that reappears from the solution on cooling
Mother liquor	A solution left after crystallization

Suspension	Fine particles that are held in a liquid and do not sink to the bottom.
Distillate	Fraction that condenses after distillation.
Miscible	Liquids that mix together
Immiscible	Liquids that do not mix and which can be separated by a separating funnel
Fraction	A distillate between a certain boiling point range separated by fractional distillation
Sublimate	Condensed solid formed during sublimation

PRACTICE EXERCISE

30 mins
Time Yourself

1. Which of the following technique is used for the separation of insoluble particles from liquids?
(a) Filtration (b) Crystallization
(c Solvent extraction (d) Chromatography

2. Which of the following way in used for classification of chromatography?
(a) Shape (b) Phase
(c) Mechanism (d) All

3. Fluted filter paper is used to
(a) Filter hot solution (b) Avoid premature crystallization
(c) Increase the rate of filtration (d) Decrease the area

4. Safe and the most reliable method of drying crystals is through
(a) Filter paper (b) Vacuum desiccators
(c) Oven (d) None of these

5. A substance having very high vapour pressure at its melting point , on heating will show
(a) Melting (b) Sublimation
(c) Decomposition (d) Condensation

6. A process controlled by Distributive law is
(a) Crystallization (b) Sublimation
(c) Solvent extraction (d) Filtration

7. A technique of partition chromatography in which the solvent is in a pool at the bottom of container
(a) Adsorption chromatography (b) Ascending chromatography
(c) Radial chromatography (d) Descending chromatography

8. Different components of a mixture have different R_f values due to
(a) Polar solvent used
(b) Combination of solvents used
(c) Their different distribution coefficients in the solvent
(d) Distributive law

9. Branch of chemistry that deals with the complete qualitative and quantitative analysis of a substance is
(a) Stoichio chemistry (b) Physical chemistry
(c) Analytical chemistry (d) Quantum chemistry

10. Identification of the components of a sample is
(a) Quantitative analysis (b) Qualitative analysis
(c) Stoichiometry (d) Physical chemistry

11. Estimation of amounts of different components in a sample is
(a) Quantitative analysis (b) Qualitative analysis
(c) Stochiometery (d) Physical chemistry

12. The technique used to separate components of mixture in solid phase.
(a) Crystallization (b) Filtration
(c) Sublimation (d) Solvent extraction

13. The solid which is left over the filter paper as a result of filtration
(a) Insoluble particles
(b) residue
(c) crystals
(d) mud

14. Size of filter paper is selected according to the amount of
(a) solution
(b) amount of insoluble solute
(c) amount of soluble solute
(d) Amount of solvent

15. Gooch Crucibles are made up of
(a) plastic
(b) fibre
(c) porcelain
(d) steel

16. Rate of filtration can be increased by applying gentle suction
(a) Gooch crucible
(b) Filter paper
(c) Sintered crucible
(d) All of the above

17. Sintered crucible is made up of
(a) Plastic
(b) glass
(c) porcetain
(d) fiber

18. The tip of funnel should touch the wall of the breaker in order to avoid
(a) Inconsistent flow of filtration
(b) splashing
(c) premature crystallization
(d) all of above

19. Separation of a solid from its hot saturated solution by cooling is called
(a) vapourization
(b) solvent extraction
(c)filtration
(d) crystallization

20. In crystallization, if the solvent is inflammable then direct heating is
(a) needed
(b) avoided
(c) depends on temperature
(d) crystallization does not involve heating

21. Which of the following technique is simple and efficient to purify a substance
(a) Filtration
(b) Sublimation
(c) Crystallization
(d) Solvent extraction

22. In solvent extraction, ether is used to separate products of organic synthesis from
(a) water
(b) iodine
(c) hydrochloric acid
(d) gases

23. 95% ethanol is called
(a) methylated spirit
(b) wood spirit
(c) rectified spirit
(d) absolute alcohol

24. The use of $CaCl_2$ and PCl_5 in the process of crystallization is as a
(a) oxidizing agent
(b) reducing agent
(c) drying agent
(d) colouring agent

25. Ratio of the amount of solute in organic and aqueous solvent is
(a) Retardation factor
(b) Distribution co-efficient
(c) Distribution in aqueous solution
(d) All statements are wrong

26. Without suction pump, filtration is
(a) Fast process
(b) Slow process
(c) Rapid process
(d) All are possible

27. Animal charcoal adsorbs the coloured
(a) impurities
(b) crystals
(c) solvents
(d) both a & b

28. Direct conversion of solids into vapours is called
(a) Solvent extraction
(b) sublimation
(c) crystallization
(d) vaporization

29. Crystallization does not involve
(a) heating (b) sublimation
(c) cooling (d) vaporization

30. In CCl_4, I_2 shows
(a) Red colour (b) Purple colour
(c) Blue colour (d) Yellow colour

31. Repeated extraction using small portions of solvents is more
(a) Reliable (b) Efficient
(c) Rapid (d) slow

32. Silica gel and alumina are used as
(a) Mobile phase (b) Stationary phase
(c) Mixed phase (d) Single phase

33. Shaking two immiscible liquids increases
(a) Length of contact (b) Volume of contact
(c) Area of contact (d) All of above

34. The solvent or mixture of solvents used for separation of compounds is called
(a) Stationary phase (b) Mobile phase
(c) Dynamic phase (d) Static phase

35. Which is not a sublime material
(a) Iodine (b) Benzoic acid
(c) Ammonium chloride (d) Potash alum

36. Sintered glass is a porous material used for
(a) absorption (b) adsorption
(c) filtration (d) sublimation

37. Selection of filter paper depends on size of particles to be
(a) filtered (b) dried
(c) decolorized (d) decanted

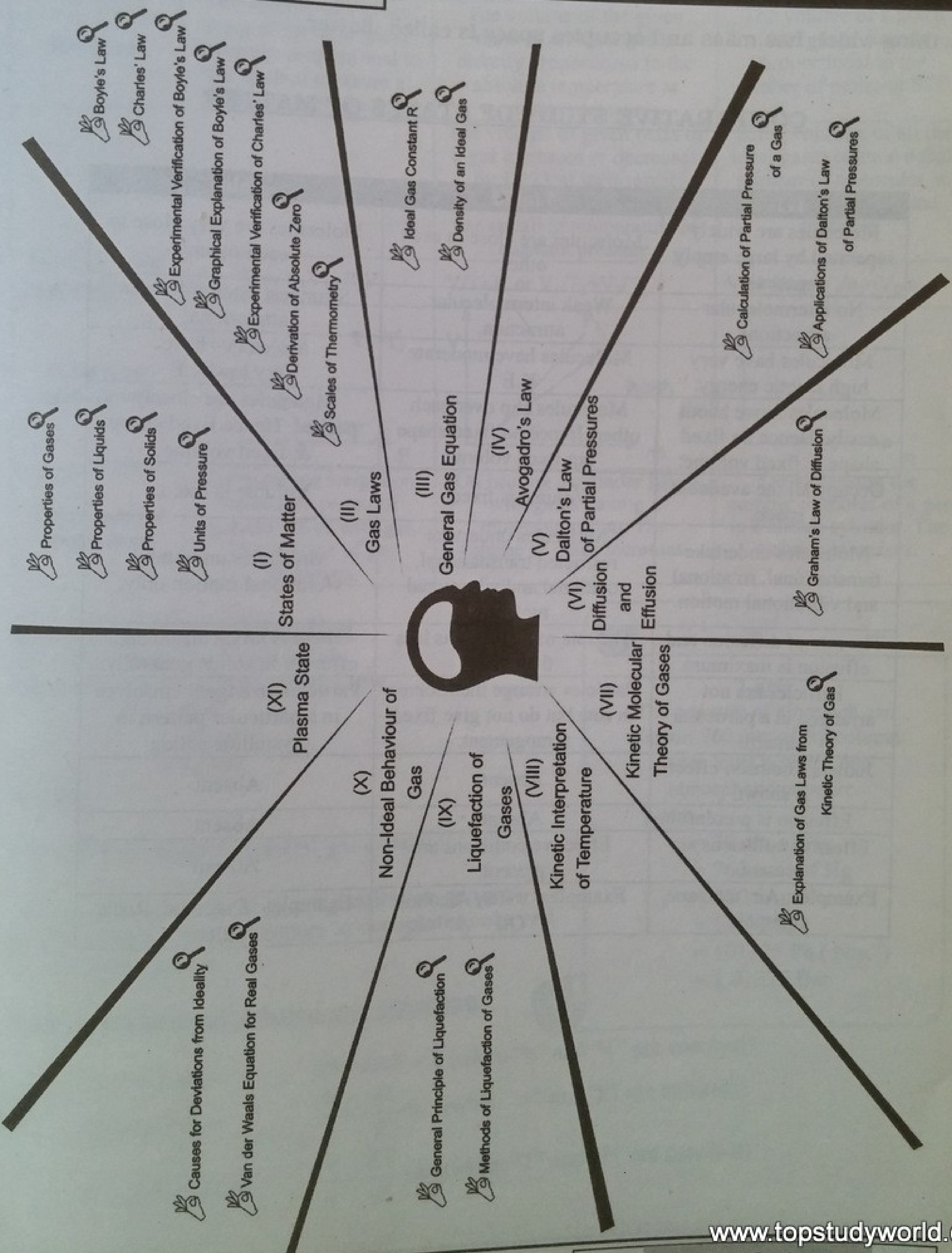
38. The solution remaining after the formation of crystals is called
(a) Mother liquor (b) Dilute solution
(c) Residue (d) both a & b

39. Which is not related pair of term used in analytical techniques
(a) Filtrate, residue (b) Sublimate, sublimiation
(c) Drying, desiccator (d) Separating funnel, mother liquor

40. The major steps involved in complete quantitative analysis are
(a) 2 (b) 3
(c) 4 (d) 5

Chapter 3

GASES


(I) States of Matter
Properties of Gases
Properties of Liquids
Properties of Solids
Units of Pressure
(II) Gas Laws
Boyle's Law
Charles' Law
Experimental Verification of Boyle's Law
Graphical Explanation of Boyle's Law
Experimental Verification of Charles' Law
Derivation of Absolute Zero
Scales of Thermometry
(III) General Gas Equation
Ideal Gas Constant R
Density of an Ideal Gas
(IV) Avogadro's Law
(V) Dalton's Law of Partial Pressures
Calculation of Partial Pressure of a Gas
Applications of Dalton's Law of Partial Pressures
(VI) Diffusion and Effusion
Graham's Law of Diffusion
(VII) Kinetic Molecular Theory of Gases
Explanation of Gas Laws from Kinetic Theory of Gas
(VIII) Kinetic Interpretation of Temperature
(IX) Liquefaction of Gases
General Principle of Liquefaction
Methods of Liquefaction of Gases
(X) Non-Ideal Behaviour of Gas
Causes for Deviations from Ideality
Van der Waals Equation for Real Gases
(XI) Plasma State

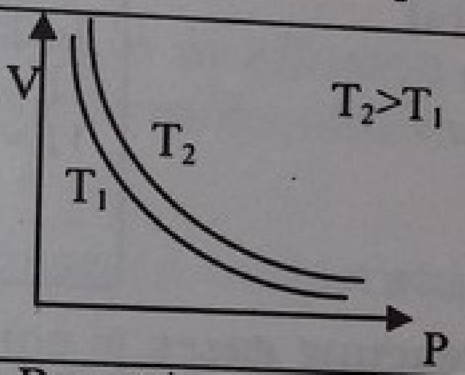
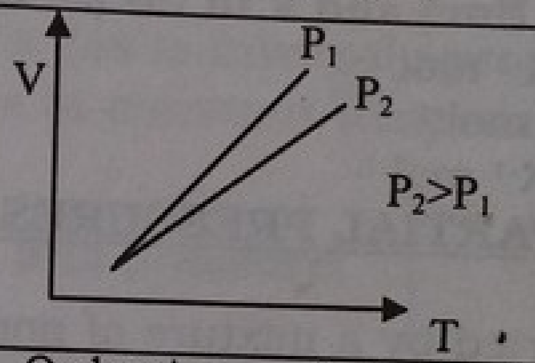
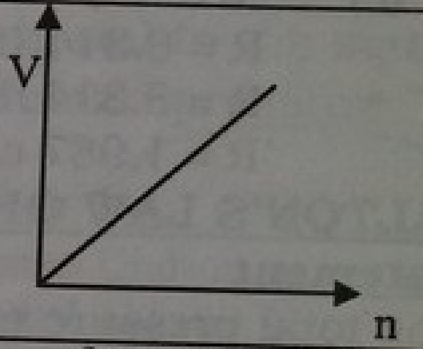
MATTER

Anything which has mass and occupies space is called matter.

COMPARATIVE STUDY OF STATES OF MATTER

Gas	Liquid	Solid
Molecules are widely separated by large empty spaces.	Molecules are close to each other.	Molecules are very close to each other.
No intermolecular attractions.	Weak intermolecular attraction.	Strongest intermolecular attractions.
Molecules have very high kinetic energy.	Molecules have moderate K.E	Molecules have Very low K.E
Molecules move about easily. Hence no fixed shape & fixed volume.	Molecules slip over each other. Hence no fixed shape but fixed volume.	Molecules are closely packed. Hence fixed shape & fixed volume.
Occupy all the available space.	Volume is fixed.	Volume is fixed.
Molecules undertake transnational, rotational and vibrational motion.	Molecules undertake restricted transnational, rotational and vibrational motion.	Molecules undertake vibrational motion only.
The rate of diffusion and effusion is maximum.	The rate of diffusion is less than gas.	There is no diffusion and effusion in solids generally.
Particles are not arranged in a particular pattern.	Particles arrange themselves in row but do not give fixed arrangement.	Particles arrange themselves in a particular pattern in crystalline solids.
Joule's Thomson effect is shown	Absent	Absent
Effusion is present	Absent	Absent
Effective collisions are present.	Effective collisions are present.	Absent
Examples: Air, methane, ammonia	Examples: water, Alcohol. Oil	Examples: Diamond, Rock, Salt.

GAS LAWS

Particulars	Boyle's law	Charles's law	Avogadro's law
Statement	The volume of a given mass of an ideal gas is inversely proportional to the applied pressure at constant temperature.	The volume of the given mass of an ideal gas is directly proportional to the absolute temperature at constant pressure	The volume of a given ideal gas is directly proportional to the number of moles at STP.
		The volume of given mass of a gas increases or decreases by 1/273 of its original volume at 0°C for every 1°C rise or fall in temperature at constant pressure	Equal volumes of all the ideal gases contain equal number of molecules at same temperature and pressure.
Mathematical representation	PV=K or $P_1V_1=P_2V_2$	V/T=K or $V_1/T_1=V_2/T_2$	V/n=K or $V_1/n_1=V_2/n_2$
Graphical verification			
Experimental observation	By putting a weight on moveable piston of cylinder filled with gas. The volume of gas decreases.	On heating a cylinder filled with gases having a moveable piston. The volume of gases increases.	On increasing the number of moles of a gas in a closed cylinder. The volume increases.

GENERAL GAS EQUATION

On combining the Boyle's law, Charles's law and Avogadro's law,

PV=K

V/T=K

V/n=K

we get

PV = nRT (R is called general gas constant)

This is called an ideal gas equation or general gas equation. This equation is completely obeyed by the ideal gases.

1-atm

The pressure of air which can support 760 mm of Hg column at sea level is called one atmospheric pressure.

1-atm
= 76 cm of Hg
= 760 mm of Hg
= 760 torr
= 14.7 PSI
= 101325 Pa (Nm^{-2})
= 1.01325 Bar

Rearrangement of general gas equation

Boyle's law	PV=nRT = k (when "n" and "T" are constant)
Charles's law	$\frac{V}{T}=\frac{nR}{P}=k$ (when "n" and "P" are constant)
Avogadro's law	$\frac{V}{n}=\frac{RT}{P}=k$ (when "T" and "P" are constant)

IDEAL GAS CONSTANT(R)

The value of R depends upon the units chosen for pressure, volume and temperature. It is independent of the nature of gas.

The value of "R" can be derived by using general gas equation.

$$PV = nRT$$

$$R = PV/nT$$

UNITS OF R

(a) **When P is in atm and V in dm^3**

$R = 0.0821\ dm^3\ atm\ K^{-1}\ mol^{-1}$

(b) **When P is in mm Hg or torr and V in dm^3 or cm^3.**

$R = 62.4 dm^3\ mm\ Hg\ K^{-1}\ mol^{-1}$

$R = 62400\ cm^3\ torr\ K^{-1}\ mol^{-1}$

(c) **When P is in Nm^{-2} and V in m^3 (SI units)**

$R = 8.314 NmK^{-1}\ mol^{-1}$

$R = 8.314 JK^{-1}\ mol^{-1}$

$R = 1.987\ calK^{-1}\ mol^{-1}$.

$1\ m^3 = 1000\ dm^3$

$1 dm^3 = 1000\ cm^3$

$1 dm^3 = 0.001\ m^3$

$1 cm^3 = 0.001 dm^3$

$1 cm^3 = 10^{-6}\ m^3$

$1 Nm = 1J$

$1 cal. = 4.18J$

$1J = 0.239\ cal$

$1J = 10^7\ ergs$

DALTON'S LAW OF PARTIAL PRESSURES

Statement

"The total pressure exerted by a mixture of non-reacting gases is equal to the sum of their individual partial pressures"

Mathematical Form

$P_{total} = P_1 + P_2 + P_3 + \ldots\ldots\ldots\ldots\ldots\ldots$ (At constant V and T)

Where $P_1, P_2, P_3 \ldots\ldots$ refer to the pressures of each individual gas.

$$P \propto n$$

The individual pressure of a gas in the mixture of gases is called its partial pressure

$$P_A = X_A P_t$$

RELATION WITH GENERAL GAS EQUATION

$$P_1 = n_1\left(\frac{RT}{V}\right), P_2 = n_2\left(\frac{RT}{V}\right), P_3 = n_3\left(\frac{RT}{V}\right)\ldots\ldots\ldots\ldots$$

Since all the gases in the mixture have same temperature and pressure, So the total pressure depends only on the total moles of gases in mixture.

$$P_{Total} = (n_1 + n_2 + n_3 + \ldots\ldots\ldots)\frac{RT}{V}$$

$$P_t = n_t\frac{RT}{V}$$

$$P_t V = n_t RT$$

$$\mathbf{P_t \propto n_t}$$

PARTIAL PRESSURE OF A GAS

$$P_t V = n_t RT$$

$$p_A V = n_A RT$$

$$p_B V = n_B RT$$

$$p_A = x_A P_t$$

$$\mathbf{p_A \propto x_A}$$

$$\mathbf{p_B \propto x_B}$$

Mole Fraction (x)

The number of moles of the component divided by the total number of moles in the mixture.

$$\text{Mole Fraction} = \frac{\text{Moles of component}}{\text{Total mole in mixture}}$$

- X of any gas in mixture is always less than unity.
- The sum of mole fractions is always equal to unity.

Conclusion

Partial pressure of a gas is the mole fraction of that gas multiplied by the total pressure exerted by the mixture of gases.

Applications Of Dalton's Law

- In calculation of P_x of dry gas collected over water.
  $P_{dry} = p_{moist} - p_{w.vap}$(aqueous tension)
- In respiration (P_{O_2} in air=159torr, P_{O_2} in lung=116torr)
- In maintaining P_{O_2} in pilot cabin
- In respiratory cylinder of sea divers

Deep Sea divers use the mixture of helium 80% and oxygen 20%

GRAHAM'S LAW OF DIFFUSION

Statement

"The rate of diffusion or effusion of a gas is inversely proportional to the square root of its density or molecular mass at constant temperature and pressure."

Rate $\alpha \frac{1}{\sqrt{d}}$ (at constant temperature and pressure)

Comparing the two gases at same temperature and pressure,

The Graham's law will be

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

OR

$$(r_1/r_2 = (d_2/ d_1)^{1/2}$$

Thomas Graham was Scottish chemist. He introduced this law in 1846

Diffusion
Diffusion is the mixing of different gas molecules by random motion under condition where molecular collisions occur.
Effusion
It is the escape of a gas through a pinhole without molecular collisions.

Application

The mixture of gases can be separated into their pure components by taking the advantage of the different rate of diffusion of the components.

KINETIC THEORY OF GASES (KMT)

Name of Scientist	Contribution
Bernoulli	Founder of KMT
Clausius	Derived Kinetic equation and deduced all the gas laws from KMT
Maxwell	Parented the law of distribution of velocities
Boltzman	Studied the distribution of energies among the molecules
van der Waal	Corrected the pressure and volume factors in ideal gas equation to make it applicable to the real gases.

Postulates of kinetic molecular theory

- Every gas consists of large number of very small particles called molecules. Gases like He, Ne Ar have mono-atomic molecules.
- The molecules of gas move haphazardly, colliding among themselves and with the walls of container changing their directions.
- The pressure exerted by the gas molecules is due to the collision of its molecules with the walls of container. The collisions among the molecules are perfectly elastic.
- The molecules of the gases are widely separated from one another and there are sufficient empty spaces among them.
- The molecules of the gases have no forces of attraction for each other
- The actual volume of molecules of a gas is negligible as compared to the volume occupied by the gas
- The motion imparted to the molecules by gravity is negligible as compared to the effect of the continued collisions between them
- The average kinetic energy of the gas molecules varies directly as the absolute temperature of the gas.

CLAUSIUS KINETIC ENERGY EQUATION

$$PV = \frac{1}{3}mN\overline{c^2}\ (\overline{c^2}\text{ is called mean square velocity})$$

RELATIONSHIP BETWEEN THE ABSOLUTE TEMPERATURE AND VELOCITIES OF GAS MOLECULES:

According to Maxwell distribution law of velocities.

- Root mean square velocity (C_{rms}) = $\sqrt{\frac{3RT}{M}}$
- Average velocity (V_{av}) = $\sqrt{\frac{8RT}{\pi M}}$
- Most probable velocity = $\sqrt{\frac{2RT}{M}}$

KIPS CREATION

Determine the average speed of a helium atom at room temp

$$C_{rms} = \sqrt{\frac{3RT}{M}}$$

$$M = 4\text{x}10^{-3}\text{Kg/mol}$$

CONCLUSIONS

- In gases and liquids, temperature is the measure of average translational kinetic energy of the molecules
- In solids, temperature is the measure of average vibrational kinetic energies of molecules.
- The average transnational kinetic energy of gas molecules is directly proportional to the Kelvin temperature of a gas i.e.

  $$E_k \ \alpha \ T$$
- When heat flows from one body to another, the molecules in the hotter body give up some of their kinetic energy through collisions to the molecules in the colder body.

NOTE:-
Kinetic equation of gases can be employed to justify all the gas laws. In other words it proves the gas laws to get their explanation from kinetic theory of gases.

ABSOLUTE ZERO

The temperature at which motion of molecules ceases.

$$0\text{K} = -273.16^\circ\text{C} = -459^\circ\text{F}$$

The absolute temperature is unattainable and the current attempts resulted in temperature as low as 10^{-5}K

LIQUEFACTION OF GASES

Liquefaction of gases is the process by which substances in their gaseous state are converted to the liquid state. When pressure on a gas is increased, its molecules come closer together, and its temperature is reduced to its critical temperature, at which P.E dominates over K.E to change it from gaseous to the liquid state.

Methods for Liquefaction of Gases

- Faraday's method (cooling is done through freezing mixture)
- Lind's method (sudden expansion of a gas to a region of low pressure)
- Claud's method (gas is allowed to do some mechanical work)

IMPORTANT TERMS

Critical temperature	It is the highest at which a substance can exist as a liquid, is called its critical temperature (T_C).
Critical pressure	It is the pressure which is required to bring about liquefaction of a gas at its critical temperature (T_C)

Joule Thomson Effect

Sudden expansion of a gas into a region of low pressure causes cooling.

NOTE

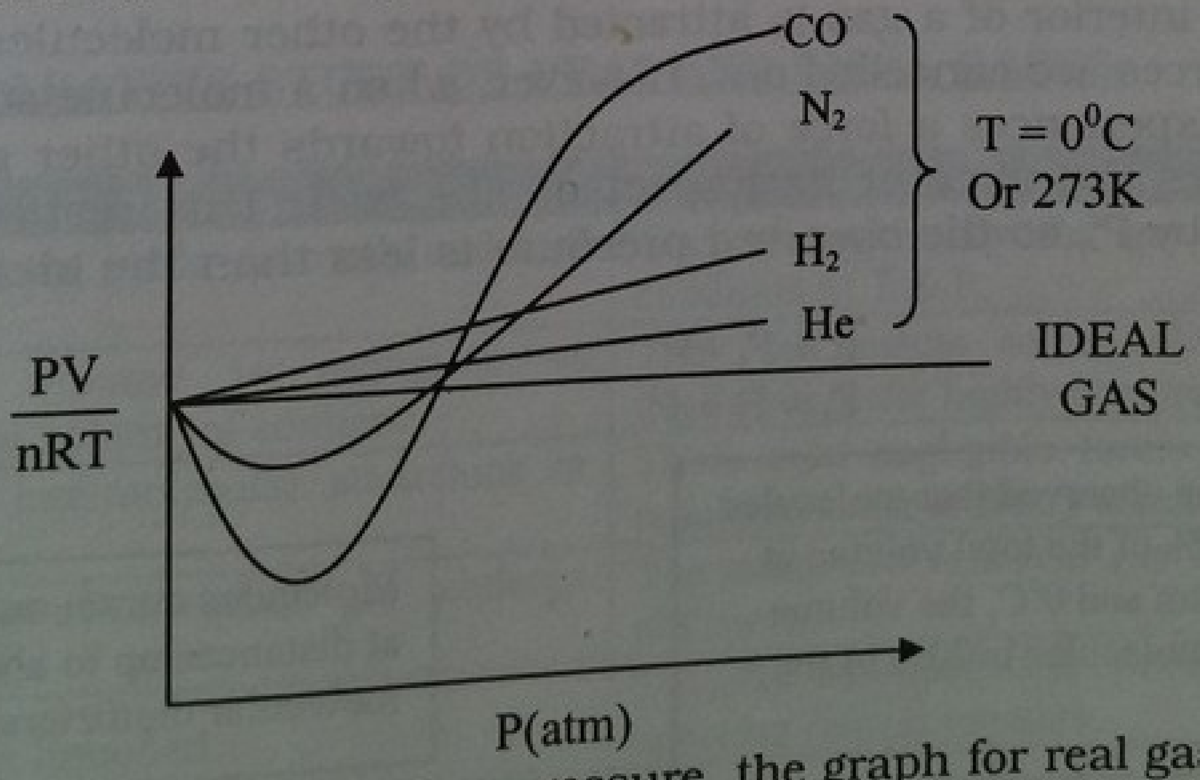
This effect is the basis of Lind's method of liquefaction.

Factors Affecting the Critical Temperature

- Size of the molecule.
- Shape of the molecule.
- Intermolecular forces among the molecules.

NON- IDEAL BEHAVIOR OF GASES

- If a graph is plotted between pressure on x-axis and the $\frac{PV}{nRT}$ (compressibility factor or Z) on y-axis for an ideal gas, a straight line parallel to the pressure axis is obtained.
- For real gases (non-ideal gases), the graph is no more parallel to the pressure axis.



- At high temperature under low pressure, the graph for real gases come closer to the expected straight line.

- If $Z = 1$ then line would be parallel to x-axis.
- If $Z < 1$ then the line obtained will below the line of ideal gas which means that there is larger decrease in volume of the gas than predicted by general gas equation due to the appearance of attractive forces present among the molecules
- If $Z > 1$ then the line obtained will be above the line of an ideal gas which means that there is less decrease in the volume of the gas than predicted by the general gas equation due to appearance of repulsive forces present among the molecules

Conclusion

(i) Gases are ideal at low pressure and non-ideal at high pressure.
(ii) Gases are ideal at high temperature and non-ideal at low temperature.

VAN DER WAAL'S EQUATION FOR REAL GASES

The real gases deviate from ideal behavior due to two faulty assumptions of KMT of gases.

These are;

(i) The volume of the gas molecules themselves is negligible as compared to the total gas volume.
(ii) There are no attractive forces among the molecules of a gas.

Experimental Observation and Volume Correction

When a gas is highly compressed then the whole volume of the container is not available to molecules because of their actual volume together with their effective volume which is not negligible under this condition. So we have to exclude this volume.

Actual volume of one mole of gas molecule = V_m

Effective volume of one mole of gas molecules = b

so,

$$b = 4V_m$$

$$V_{free} = V_{vessel} - b$$

Microscopic Study of Gas and Pressure Correction

When pressure on the gas is increased and its temperature is decreased the molecules come close to each other which results in the appearance of attractive forces among gas molecules.

A molecule in the interior of a gas is attracted by the other molecules on all sides so these attractive forces are cancelled out. However, when a molecule strikes the wall of the container, it experiences a force of attraction towards the other molecules in the gas. This decreases the force of its impact on the wall. This results a decrease in pressure denoted by P'. so the observed pressure is less than the ideal pressure P_i by an amount P'.

$$P = P_i - P'$$

$$P_i = P + P'$$

For real gases, it is observed that molecules occupy only 0.05% of the total volume at STP, but at 500 atm and 0°C, the volume occupied by gas molecules is 20% of the total volume.

Molecules attract one another at distances up to about 10 molecular diameters.

Mathematical Representation

Both these corrections can be represented mathematically by the modification of the general gas equation called the van der Waal's equation.

- The increase in V caused by the effect of molecular volume is corrected by subtracting an amount nb from the observed volume. i.e.
  $V\text{-}nb$
- The change in pressure caused by the effect of intermolecular attractions is best corrected by adding an amount an^2/v^2 to the pressure.

Correction for intermolecular attraction

Correction for molecular volume

Van der Waal's equation $\left(P+\frac{an^2}{V^2}\right)(V\text{-}nb) = nRT$

For n moles of gas $P = \frac{nRT}{V\text{-}nb} - \frac{an^2}{V^2}$

For one mole of gs $P = (RT/V\text{-}b) - a/V^2$

Here "a" and "b" are called Van der Waal's constant.

Units of (a)

(i) $Nm^{+4}\ mol^{-2}$ (S.I Units)
(ii) atm $dm^6\ mol^{-2}$ (other common units)

Units of (b)

(i) $m^3\ mol^{-1}$ (S.I Units)
(ii) $dm^3\ mol^{-1}$ (other common units)

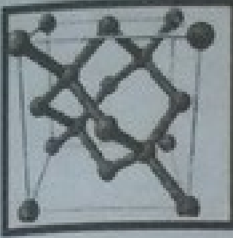
COMPARATIVE STUDY OF REAL AND IDEAL GASES

Ideal Gases	Real Gases
Ideal gas obeys the gas laws strictly under all T & P.	They do not obey the gas laws under all condition of T & P.
Their actual volume is negligible as compared to the volume of container.	They do possess some volume that is not negligible under highly compressed state.
There are no intermolecular attractions or repulsions.	There exist negligible forces of attraction or repulsion under ordinary conditions.
The molecules of an ideal gas undergo elastic collisions.	The molecules of a real gas undergo inelastic collisions.
They can not be liquefied.	They can be liquefied at critical temperature by applying critical pressure.

PLASMA STATE

The most primitive state of matter which is ionized gas mixture consisting of ions, electrons and neutral atoms is called plasma state.

- Plasma was identified by an English scientist William Crooks in 1979.
- Plasma is estimated to constitute more than 99% of the visible universe.
- Artificial plasma can be created by using electrical charges on a gas.
- Natural plasma exist only at very high temperature or low temperatures Vacuums.
- It shows a collective response to electric and magnetic fields.
- It is macroscopically neutral.
- It has a lot of important technological applications.



PRACTICE EXERCISE

30 mins
Time Yourself

1. What is the relative rate of effusion of CO and CO_2?
   (a) CO is 1.25 times faster than CO_2
   (b) CO is 3.75 times faster than CO_2
   (c) CO_2 is 1.25 times faster than CO
   (d) Both diffuse at the same rate
2. Which of these gases diffuse more quickly than oxygen?
   (a) H_2S
   (b) NO
   (c) Cl_2
   (d) N_2O
3. Which of the following is not considered as an intermolecular force between molecules?
   (a) Coordinate covalent bonds
   (b) Hydrogen bonds
   (c) Debye forces
   (d) London dispersion forces
4. The weakest (in strength) of the following intermolecular forces is
   (a) Hydrogen bonding
   (b) Vander Waal's forces
   (c) Forces among the polar molecules
   (d) Ionic bond
5. Ideal gasses have all the following characteristics except.
   (a) Absence of intermolecular forces
   (b) Collisions among the molecules of an ideal gas are perfectly elastic
   (c) The molecules occupy no space
   (d) All of the above are correct
6. Which of the following statements is true about plasma
   (a) It may be the first state of matter.
   (b) It is not a phase transition.
   (c) It is a conductor of electricity.
   (d) All of the above
7. Which statement is correct
   (a) $PV_m \, \alpha \, T$
   (b) $P \, \alpha \, CT$
   (c) $PM \, \alpha \, dT$
   (d) All above
8. Under what conditions the gases deviate from the ideal behavior?
   (a) High temperature
   (b) Low temperature
   (c) High pressure
   (d) b and c
9. Which one has the lowest density at room temperature?
   (a) Ne
   (b) N_2
   (c) NH_3
   (d) CO
10. The introduction of Kelvin scale in thermometry is according to
    (a) Boyle's law
    (b) Charles' law
    (c) Dalton's law
    (d) Graham's law
11. 0.5 mole of nitrogen gas and 0.5 mole of carbon monoxide gas at STP have same
    (a) Value of "a"
    (b) Mass
    (c) Atoms
    (d) Both b & c
12. At constant temperature the pressure of an ideal gas is doubled, its density becomes
    (a) Half
    (b) Double
    (c) Same
    (d) None

13. The diffusion of gases at absolute zero will be
(a) Unchanged (b) Slightly decreased
(c) Slightly increased (d) Zero

14. Which of the following option is incorrect about gases?
(a) All molecules move with same speed.
(b) All molecules behave independently
(c) $PV/RT = n$
(d) All gases cannot be liquefied through Lind's Method

15. Critical temperature for different gases is different and depends upon
(a) Size of molecule (b) Shape of molecule
(c) Intermolecular attractions (d) All of the above

16. In how many forms do matter exists?
(a) Three (b) Four
(c) Five (d) Two

17. What is the simplest form of matter?
(a) Gas (b) Liquid
(c) Solid (d) Semi solid

18. What is the abundant form of matter on earth?
(a) Gas (b) Liquid
(c) Solid (d) Plasma

19. Which state of matter has the lowest density?
(a) Gas (b) Liquid
(c) Solid (d) plasma

20. What do we call to sudden expansion of plasma?
(a) Avogadro's law (b) Graham's law of diffusion
(c) Joule Thompson effect (d) Dalton's law of partial pressure

21. The solid particles only posses
(a) Translational motion (b) Vibrational motion
(c) Rotational motion (d) All of above motions

22. For a gas where volume and pressures are $1dm^3$ and 2 atm respectively, what should be its new volume, when pressure is increased to 6 atm at constant temperature?
(a) $1/2dm^3$ (b) $1/3dm^3$
(c) $1/4dm^3$ (d) $2/3\ dm^3$

23. If 1/V is plotted on X-axis and pressure on Y-axis at constant temperature what should appear
(a) Straight line parallel to x-axis (b) Straight line parallel to y-axis
(c) Straight line (d) Curve

24. The general gas equation to know the volumes of the gas at various temperatures is
(a) $V_o = \frac{273V_T}{273+T}$ (b) $V_o = V_T\left(1-\frac{T}{273}\right)$
(c) $V_T = V_0\left(1+\frac{T}{273}\right)$ (d) None of the above

25. Which one is the right value for R?
(a) 0.0821 atm $dm^3\ k^{-1}\ mol^{-}$ (b) 0.0821 atm $m^3\ k^{-1}$
(c) 2 cal $k^{-1}\ mol^{-1}$ (d) 8.314 $Nm^2\ k^{-1}\ mol^{-1}$

26. One mole of an ideal gas at 546.3 K under 2 atm pressure has a volume of
(a) 22.414 m^3
(b) 44.828 dm^3
(c) 22.414 dm^3
(d) 11.212 cm^3

27. The partial pressure exerted by the water vapours is called
(a) Surface tension
(b) Aqueous tension
(c) Vapour pressure
(d) Hydraulic pressure

28. Which one is not the partial pressure of oxygen in the lungs?
(a) 0.1526 atm
(b) 116 mm of Hg
(c) 116 torr
(d) 1 atm

29. The spreading of fragrance or scent in air is due to
(a) Diffusion
(b) Effusion
(c) Attraction with air
(d) Low dsensity

30. Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of total pressure exerted by oxygen is
(a) $\frac{1}{3}$
(b) $\frac{8}{9}$
(c) $\frac{1}{9}$
(d) $\frac{16}{17}$

31. The kinetic molecular theory of gases was put forward in 1738 by
(a) Boltzman
(b) Maxell
(c) Clausius
(d) Bernoulli

32. The expression for root mean square velocity is
(a) $C_{rms}=\sqrt{(3RT/M)^2}$
(b) $C_{rms}=\sqrt{3RT/M}$
(c) $C_{rms}=3RT/M$
(d) $C_{rms}=\sqrt{3/2RT/M}$

33. The highest temperature at which a substance can exist as a liquid is called its
(a) Critical temperature
(b) Standard temperature
(c) Absolute temperature
(d) Upper consulate temperature

34. Hydrogen effuses four times more rapidly than volume of an unknown gas, molar mass of unknown gas should be
(a) 16 $gmol^{-1}$
(b) 32 $gmol^{-1}$
(c) 48 $gmol^{-1}$
(d) 64 $gmol^{-1}$

35. What will be the pressure of 1 mole of an ideal gas maintained at 300 K and 250cm^3 volume?
(a) 98.5 atm
(b) 96.7 atm
(c) 95.8 atm
(d) 97.1 atm

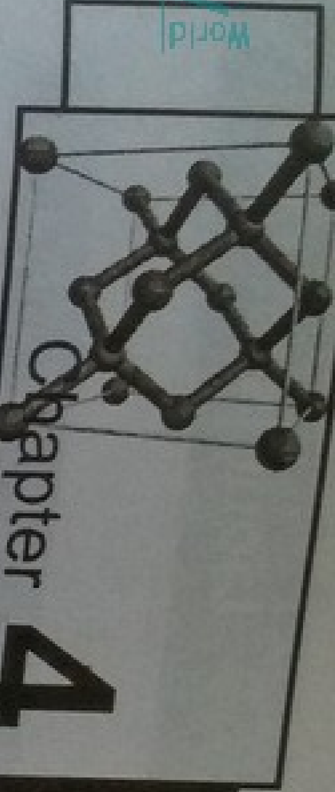
36. The processes of effusion and diffusion are best understand by
(a) Dalton's law
(b) Avogadro's law
(c) Graham's law
(d) Charles law

37. Who made volume and pressure correction to explain deviation of gases from ideal behaviour?
(a) Clausius
(b) Boltzman
(c) Charles
(d) Vander waal

38. The non-ideal behaviour results chiefly from
(a) Intermolecular attraction and infinite volume
(b) Elastic collisions and finite volume
(c) Intermolecular attractions and finite volume
(d) Intermolecular attraction only

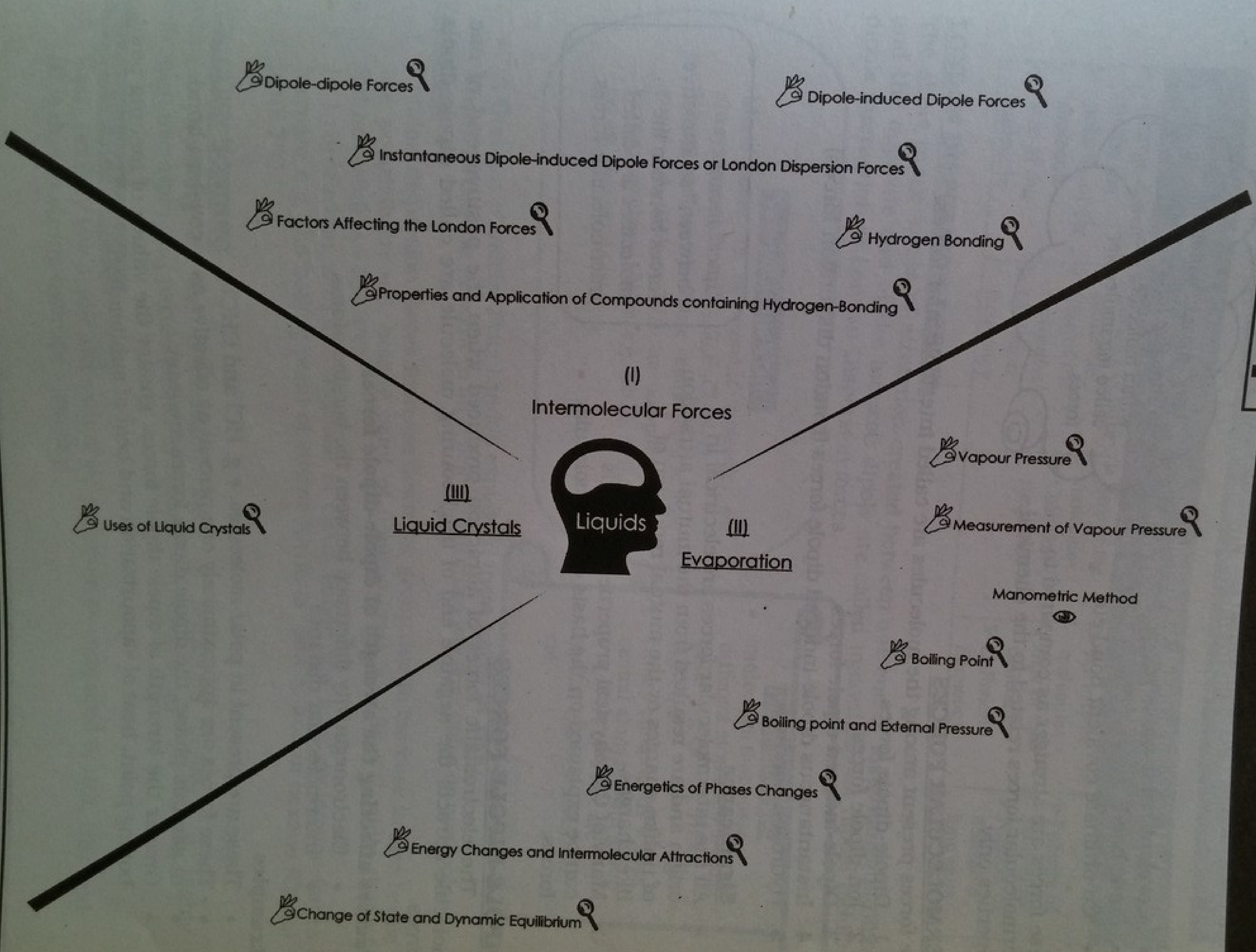
39. The gases become non-ideal at
    - (a) High temperature and high pressure
    - (b) Low temperature and low pressure
    - (c) High temperature and low pressure
    - (d) Low temperature and high pressure

40. Lind's method is employed for
    - (a) Separation of gases
    - (b) Expansion of gases
    - (c) Compression of gases
    - (d) Liquefaction of gases



Chapter 4

LIQUIDS AND SOLIDS



Liquids

(I) Intermediate Forces

- Dipole-dipole Forces
- Dipole-induced Dipole Forces
- Instantaneous Dipole-induced Dipole Forces or London Dispersion Forces
- Factors Affecting the London Forces
- Hydrogen Bonding
- Properties and Application of Compounds containing Hydrogen-Bonding

(II) Evaporation

- Vapour Pressure
- Measurement of Vapour Pressure
  - Manometric Method
- Boiling Point
- Boiling point and External Pressure
- Energetics of Phases Changes
- Energy Changes and Intermolecular Attractions
- Change of State and Dynamic Equilibrium

(III) Liquid Crystals

- Uses of Liquid Crystals

INTRAMOLECULAR FORCES

The forces, which are present within the molecules, are called intramolecular forces e.g.

- Covalent bond
- Ionic bond
- Co-ordinate covalent bond etc.

These forces are stronger as compared to intermolecular forces related to the chemical properties only.

> "Intra" means "within" so attractive forces within molecules are called intramolecular forces.

ITERMOLECULAR FORCES

The forces present among the molecules are called intermolecular forces.

1. Dipole-dipole forces
2. Ion-dipole forces
3. Dipole-induced dipole forces
4. Instantaneous dipole-induced dipole forces (London dispersion forces)
5. Hydrogen bonding

Significance

- ➢ All the intermolecular forces are electrical in origin and are resulted from the mutual attraction of unlike charges or the mutual repulsion of like charges.
- ➢ Many of the physical properties of liquids can be explained on the basis of intermolecular forces.

> "Inter" means "between" so attractive forces between the molecules are called intermolecular forces.

DIPOLE-DIPOLE FORCES

The electrostatic forces of attraction produced when the positive end of one molecule attracts the negative end of neighbouring molecule are called dipole dipole forces.

Factors affecting the strength of dipole-dipole forces

- Electronegativity difference between the bonded atoms
- Intermolecular distance

Examples

- These are present in polar molecules. e.g. HCl and $CHCl_3$
- These forces are approximately one percent as effective as a covalent bond.
- In gaseous phase, the dipole dipole forces are least.
- Greater the strength of dipole dipole forces, greater the values of melting point, boiling point, heat of vapourization and heat of sublimation.

Factors Affecting the Strength of Intermolecular Forces

Ion-dipole force	Dipole-induced dipole force	London dispersion forces	Dipole-dipole forces	Hydrogen bond
➢ Charge density of the ion ➢ polarity of the molecule ➢ size of the molecule	➢ Polarity of polar molecule ➢ Size of the molecules ➢ Collision frequency	➢ Size of the molecules ➢ Collision frequency	➢ Polarity of molecules ➢ Size of the molecules ➢ Collision frequency	➢ Polarity of molecules ➢ Number of utilizable lone pairs

LONDON DISPERSION FORCES

The short range forces of attraction created between one end of instantaneous dipole and the opposite end of the induced dipole are called instantaneous dipole induced dipole interaction or London Dispersion forces.

Non-polar molecules

- Mono-atomic or homoatomic molecules are always non-polar e.g. H_2, O_2, F_2, Cl_2, N_2 etc.
- Binary compounds whose central atom is from group IIA, IIIA or IVA are non-polar. They have symmetrical shape. e.g. $BeCl_2$, BH_3, CCl_4 etc are also non-polar.

Polar molecules

- molecules that posses different atoms are usually polar. e.g CH_3Cl, HOCl, H_2SO_4 etc.
- Binary compounds whose central atom is from group VA, VIA or VIIA are dipolar e.g. H_2S, HCl, HF etc.

- A German physicist Fritz London explained these forces in 1930.
- These forces are present in all types of molecules whether polar or non-polar.

Variations

- London dispersion forces increase down the group due to increase in size hence the polarizibility e.g. boiling point of fluorine (gas) is −188.1°C while that of iodine (solid) is +184.4°C.
- In hydrocarbon with the increase of chain length the inter molecular forces increase e.g. the boiling point of ethane (C_2H_6) is -88.6°C and of hexane (C_6H_{14}) is 68.7°C.

HYDROGEN BONDING

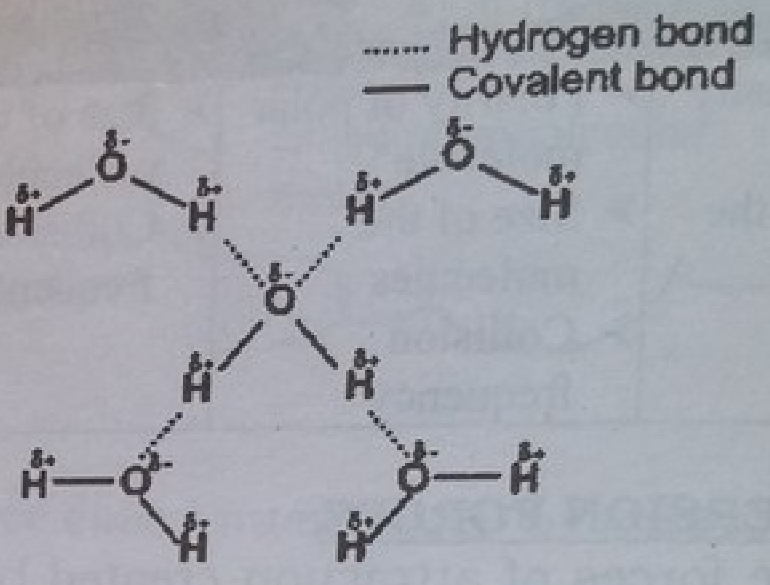
Hydrogen bonding is the electrostatic force of attraction between a highly electronegative atom and partial positively charged hydrogen atom.

Points to be Remembered

- Exceptionally low acidic strength of HF molecule as compared to HCl, HBr and HI is due to strong hydrogen bonding.

- Ammonia and hydrogen fluoride can form only one hydrogen bond due to presence of only one utilizable lone pair of electrons and one utilizable H-atom respectively.
- Water can form two hydrogen bonds as it has two utilizable hydrogen atoms and two utilizable lone pairs on oxygen atom.

The strength of hydrogen bond is generally twenty times less than that of a covalent bond.



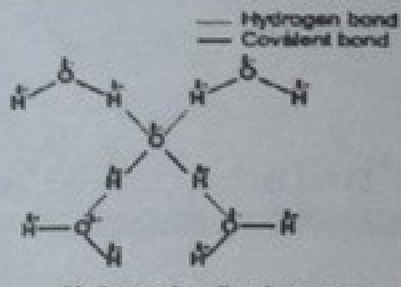
Hydrogen bonding in water.

A COMPARISON OF INTER-MOLECULAR FORCES

Forces	Strength	Characteristics
Ion –dipole	Moderate (10-50kJ/mol)	Occurs between ions and polar solvents
Dipole-dipole	Weak (3-4KJ/mol)	Occurs between polar molecules
London dispersion	Weak (1-10KJ/mol)	Occurs between all molecules
Hydrogen bond	Moderate (10-40KJ/mol)	H and N or O or F usually

PROPERTIES OF COMPOUNDS CONTAINING HYDROGEN BOND

Property	Description
Thermodynamic properties of covalent hydrides	▪ Greater the E.N difference, stronger will be hydrogen bond. Compounds with such condition have higher B.P than those molecules, which does not have such property. ▪ In HF and H_2O, more E.N difference is between H and F than H and O, but water has high B.P than HF, it is due to greater number of H-bonds between water than in HF.
Application in biological compounds	**Fiber proteins** Fiber proteins consist of large chains of amino acids and these chains are coiled about one another into a spiral. This spiral is called helix. Such a helix may either be right handed or left handed (α-helix & β-helix). In both cases >NH and >CO adjacent to one another are linked together by H-bond. **DNA** Deoxyribonucleic acid (DNA) has two spiral chains. These are coiled about each other and are linked together by H-bond between the nitrogenous bases i.e. A=T & G≡C and give rise to double helical structure. **Food Material** The food materials like carbohydrates e.g. glucose, fructose and sucrose have –OH groups which are responsible f[illegible] them.

Clothing	Hydrogen bonding is involved in thread.
Solubility	▪ Compound with hydrogen bond is soluble in compound having hydrogen bond e.g. H_2O and C_2H_5OH are soluble with each other.
Cleaning action	▪ Soaps and detergents perform the cleansing action because the polar part of their molecules are water soluble due to hydrogen-bonding and the non-polar parts remain outside water, because they are alkyl or benzyl portions and are insoluble in water.
Hydrogen bonds in paints and dyes	▪ The adhesive property of paints and other dyes like glue etc. is due to hydrogen bond.
Structure of ice  Hydrogen bonding in water.	▪ In ice, the oxygen atom of water molecule is surrounded by four H-atoms. The two H atoms are linked through covalent bond while the other two H-atoms are linked through H-bond. This is extended throughout creating the empty spaces in the structure. That is why when water freezes it occupies 9% more space and its density decreases. That's why ice floats on the surface of water.

ENERGETICS OF PHASE CHANGE

Particulars	Description
Enthalpy change	At constant P, heat change during the process in which physical or chemical change occur is called enthalpy change (ΔH).
Molar heat of fusion	It is the amount of heat absorbed by one mole of a solid when it melts into liquid form at its melting point. The pressure, during the change is kept one atmosphere. P (1atm). It is denoted by ΔH_f.
Molar heat of vaporization	It is the amount of heat absorbed when one mole of a liquid is changed into vapours at its boiling point. The pressure, during the change is kept one atmosphere. It is denoted by ΔH_v.
Molar heat of sublimation	It is the amount of heat absorbed when one mole of a solid sublimes to give one mole of vapours at a particular temperature and one atmospheric pressure. It is denoted by ΔH_s.

FACTORS AFFECTING MOLAR HEATS	
Nature of material	Polar liquids have high (ΔH_v) molar heat of vaporization than non-polar. Polar solids have high (ΔH_f) molar heat of fusion than non-polar.
Size of molecule	Larger the size of molecules, greater will be H_v

EVAPORATION

The spontaneous change of a liquid into its vapours is called evaporation and it continues at all temperatures.

Example:

$$H_2O_{(l)} \longrightarrow H_2O_{(g)} \qquad \Delta H_v = 40.7\text{kJ mol}^{-1}$$

Characteristics

It is,

- A natural phenomenon
- a cooling process
- continued at all temperature
- an endothermic process
- a surface phenomenon

Factors affecting evaporation

- surface area of the liquid
- nature of the liquid
    - ➢ size of the molecules
    - ➢ shape of the molecules
    - ➢ inter molecular forces
- temperature
- external pressure

VAPOUR PRESSURE

The pressure exerted by the vapours of a liquid in equilibrium with its liquid at a given temperature is called vapour pressure.

Barometer
A device for measuring the pressure of the atmosphere.
Manometer
A device for measuring pressure of a gas or a liquid in vessel.

Factors affecting vapour pressure

- nature of the liquid
    - ➢ size of the molecules
    - ➢ shape of the molecules
    - ➢ inter molecular forces
        - o Due to weaker intermolecular forces, at 20°C vapour pressure of isopentane is more (580 torr) than glycerol (0.00016 torr)
- external pressure

Point to be remembered

- Vapour pressure of water is 4.579 torr at 0°C.
- The rate of change of a vapour pressure with temperature can be calculated by Clausius Clapeyron equation.

Measuring vapour pressure
Measurement

- Monometer is used to measure V.P.
- Thermostat is a system whose temperature can be control by means of Knob.
- Vacuum is created by vacuum pump
- Liquid is frozen and then melted, so that air can be removed

$$P = P_a + \Delta h$$

Boiling point
The temperature at which the vapour pressure of the liquid becomes equal to external pressure is called boiling point.
Boiling point depends upon external pressure.

	External Pressure	Boiling Point of H_2O
(1)	1489 torr	120°C
(2)	700 torr	98°C (Muree Hills)
(3)	323 torr	69°C (Mount Averest)
(4)	23.7 torr	25°C

The boiling point and decomposition point of glycerine is 290°C

Chapter 4

Liquids and Solids

KINDS OF PHASE CHANGES

Phase transition	Name	Examples
Solid – liquid	Fusion, melting	Melting of snow and ice
Solid – gas	Sublimation	Sublimation of dry ice
Liquid – solid	Freezing (solidification)	Freezing of water
Liquid – gas	Vapourization	Evaporation of water
Gas – liquid	Condensation or liquification	Formation of dew
Gas – solid	Condensation or solidification (Deposition)	Formation of frost or snow

DYNAMIC EQUILIBRIUM

A situation when two opposing changes occur at equal rates is called dynamic equilibrium e.g.

$$\text{ice} \xrightleftharpoons{0^\circ C} \text{water}$$

LIQUID CRYSTALS

A state that exists between two temperatures i.e. melting temperature and clearing temperature is called liquid crystals.

DISCOVERY

An Austrian botanist, Frederick Reinitzer discovered liquid crystals in 1888 while studying cholesteryl benzoate

$$\textbf{Crystal} \longrightarrow \textbf{liquid crystal} \longrightarrow \textbf{liquid}$$

$$\text{Cholesteryl benzoate} \longrightarrow 145\ {}^{0}\text{C} \longrightarrow 179\ {}^{0}\text{C}$$

Properties

- Fluidity like liquids
- Optical properties
- Isotropic

Types of liquid crystals

1. Nematic
2. Smectic
3. Cholesteric

USES OF LIQUID CRYSTALS

Usage	Description
Colour display	• Liquid crystals diffract light and imparts colour. • Colour changes with change in temperature.
Temperature sensor	• Used as temperature sensor.
Electrical circuit	• Used to detect potential failure in electric circuit.
Diagnosis	• Used to locate veins, arteries, infections and tumors. • Used in diagnosis of breast cancer.
Electrical devices	• Used in digital watches, computer and calculators
Chromatography	• Used as a solvent.
Others	• Oscillographic and TV displays use liquid crystal screen.

Chapter 4

Liquids and Solids

Solids

- (I) Introduction
  - Types of Solids
    - Crystalline Solids
    - Amorphous Solids
  - Properties of Crystalline Solids
    - Geometrical Shape
    - Melting Points
    - Cleavage Planes
    - Anisotropy
    - Symmetry
    - Habit of a Crystal
    - Isomorphism
    - Polymorphism
    - Allotropy
    - Transition Temperature
- (II) Crystal Lattice
  - Unit Cell
- (III) Crystals and Their Classification
  - Cubic System
  - Tetragonal System
  - Orthorhombic or Rhombic System
  - Monoclinic System
  - Hexagonal System
  - Rhombohedral System or Trigonal System
  - Triclinic System
- (IV) Classification of Solids
  - Ionic Solids
    - Properties of Ionic Solids
    - Structure of Sodium Chloride
    - Lattice Energy
  - Covalent Solids
    - Properties of Covalent Crystals
    - Structure of Diamond
  - Molecular Solids
    - Properties of the Molecular Solids
    - Structure of Solid Iodine
  - Metallic Solids
    - Properties of Metallic Crystals
    - Structure of Metals
- (V) Determination of Avogadro's Number (N_A)

SOLIDS

Those substances which are rigid, hard, having definite shape and definite volume are called solids.

TYPES OF SOLID

Name	Details
Crystalline solids	▪ Molecules, ions or atoms arranged in specific three-dimensional pattern e.g. NaCl, KCl, sucrose, I_2 and ice etc.
Amorphous solids (Pseudo solids)	▪ Molecules, ions or atoms do not have regular order of arrangement e.g. rubber, glue, glass etc.

PROPERTIES OF CRYSTALLINE SOLIDS

Property	Description
Geometric shape	Have definite geometry and shape.
Melting Point	Sharp melting points.
Cleavage planes	Whenever the crystalline solids are broken they do so along definite planes. These planes are called the cleavage planes.
Symmetry	▪ The repetition of faces, angles and edges when a solid is rotated by 360° along its axis is called symmetry. ▪ There are many types of symmetry elements: - ➢ Centre of symmetry ➢ Plane of symmetry ➢ Axis of symmetry
Habit of a crystal	▪ The shape of crystal in which it usually grows is called habit of a crystal.
Isomorphism	▪ The phenomenon in which two different compounds exist in the same crystalline form is called isomorphism. ▪ Many solids show isomorphism e.g. $NaNO_3$ and KNO_3 exhibit rhombohedral crystalline form.
Polymorphism	▪ The phenomenon in which one compound contains more than one crystalline forms is called polymorphism. ▪ e.g. $AgNO_3$ exists in Rhombohedral and orthorhombic from. ▪ Compounds exhibit this phenomenon.
Allotropy	▪ The phenomenon in which an element exists in more than one crystalline form is called allotropy. ▪ e.g. C exists as graphite and diamond. ▪ Elements exhibit this phenomenon.
Transition temperature	It is that temperature at which two crystalline forms of the same substance can co-exist in equilibrium with each other. ▪ Above and below this temperature only one form exists. Grey tin (cubic) $\overset{13.2^{\circ}C}{\rightleftharpoons}$ White tin (tetragonal)

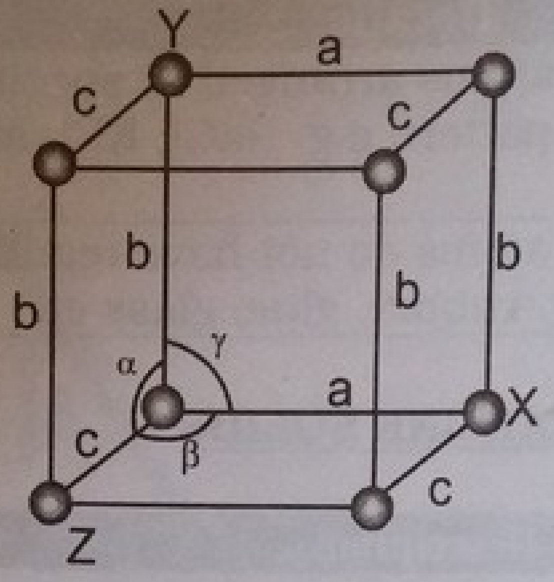
CRYSTAL LATTICE

Array of points representing atoms, ions or molecules of crystal, arranged at different sites in three dimensional space called lattice.

UNIT CELL

The smallest part of crystal lattice, that has all the characteristic features of crystal is called a unit cell.

- ➢ Unit cell contains three angles (α, β, γ) and three axis a,b,c. These six parameters are called unit cell dimensions or crystallographic elements.



Crystallography

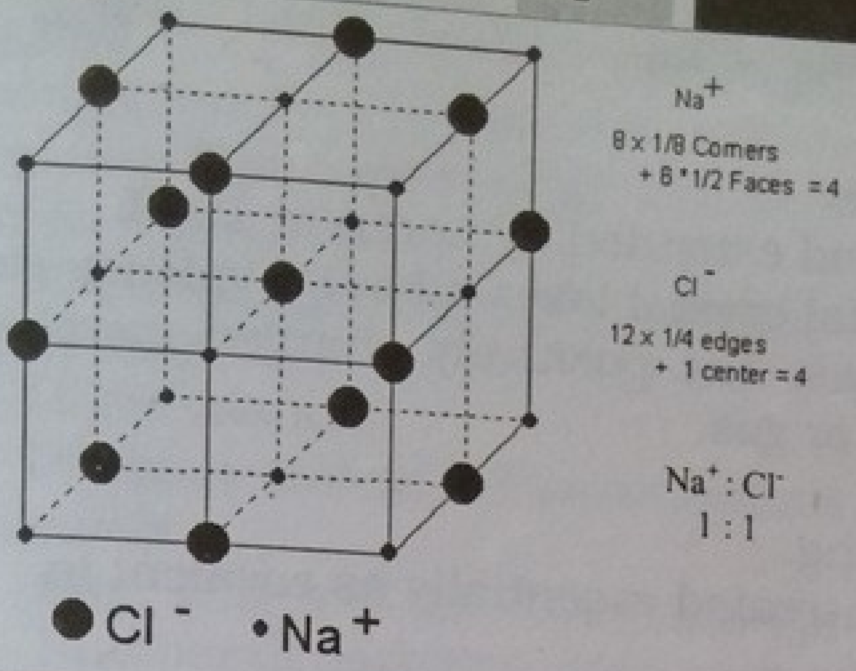
The study of the structure and properties of crystals with the help of x-rays is called crystallography.

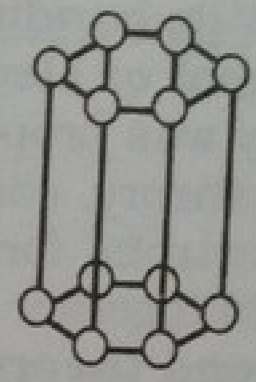
CRYSTAL AND THEIR CLASSIFICATION

- There are 230 different forms of crystals on the basis of symmetry of geometrical structures of crystals.
- The cubic system consists of three separate types of structures.
  - ➢ Simple (primitive)
  - ➢ Face centered
  - ➢ Body centered
- The basic difference between Bravis lattice are
  - ➢ Angles between the faces
  - ➢ Relative proportions of the sides
- There are 14 types of Bravis lattices.
- There are 7 crystal systems.

CRYSTAL SYSTEM

Name	Length	Angles	Examples
Cubic	a = b = c All sides equal	$\alpha = \beta = \gamma = 90^0$ All angles equal	NaCl, NaBr Diamond
Tetragonal	$a = b \neq c$ Two sides equal	$\alpha = \beta = \gamma = 90^0$ All angles equal	$BaSO_4 . 4H_2O$ SnO_2
Orthorhombic	$a \neq b \neq c$ All sides unequal	$\alpha = \beta = \gamma = 90^0$ All angles equal	$FeSO_4 . 7H_2O$ $ZnSO_4 . 7H_2O$
Trigonal or Rhombohedral	a = b = c All sides equal	$\alpha = \beta = \gamma$ Each angle between 90^0 to 120^0	$NaNO_3$ KNO_3
Hexagonal	$a = b \neq c$ Two sides equal	$\alpha = \beta = 90^0$ $\gamma = 120^0$	Graphite ZnO, CdS
Monoclinic	$a \neq b \neq c$ All sides unequal	$\alpha = \gamma = 90^0$ $\beta > 90^0$	$CaSO_4$, Borax $Na_2CO_3 . 10H_2O$
Triclinic	$a \neq b \neq c$ All sides unequal	$\alpha \neq \beta \neq \gamma$ All angles unequal	$CuSO_4 . 5H_2O$ $K_2Cr_2O_7$





Hexagonal crystal

Some important points are as follows:

NaCl

- In NaCl, each Na^+ is surrounded by six Cl^- ions.
- Distance between two consective Cl^- ions is 5.63 A°.
- In each unit cell there are four formula units = $\frac{8}{8}+\frac{6}{2}=4$ formula units

Lattice Energy

- Energy released to form one mole of ionic compound from its Gaseous ions is called lattice energy.
- With increase in the size of cation or anion, lattice energy decreases and vice versa.

Diamond

- In diamond, C atom is sp^3 hybridized and geometry is tetrahedral.
- Bond angle in diamond is 109.5°.

Type of Solid	Structural Particles	Intermolecular Forces	Typical Properties	Examples
metallic	cations plus delocalized electrons	metallic bonds	hardness varies from soft to very hard; melting point varies from low to very high; lustrous; ductile; malleable; very good conductors of heat and electricity	Na; Mg; Al; Fe; Zn; Cu; Ag; W
ionic	cations and anions	electrostatic attractions	hard; moderate to very high melting points; nonconductors of electricity (but good electrical conductors in the molten state)	NaCl; $NaNO_3$; MgO
molecular	molecules (atoms of noble gases)	london and/or dipole-dipole and/or hydrogen bonds	soft: low melting points; nonconductors of heat and electricity; sublime easily in many cases	Noble-gas elements; CH_4; CO_2; P_4; S_8;I_2;H_2O
network covalent	atoms	covalent bonds covalent bonds	very hard; very high melting points; nonconductors of electricity	C (diamond); SiC; SiO_2

METALLIC SOLIDS

Theories of metallic bonding

(a) Electron pool or electron gas theory.

This theory was proposed by Drude and extended by Loren in 1923. According to this theory, each atom in a metal crystal loses all of its valence electrons. These valence electrons form a pool or a gas. The positively charged metal ions are believed to be held together by electron pool or gas.

(b) Valence bond theory

This theory was presented by L. Pauling. According to his theory, the metallic bond is treated essentially as covalent in character.

(c) Molecular orbital theory Or band theory

According to this theory, it is assumed that the electrons in the completely filled orbitals are essentially localized, while atomic orbitals containing the valence electrons interact or overlap to form a set of delocalized orbitals. These delocalized orbitals are the molecular orbitals which extend over the entire crystal lattice. Such a combination of atomic orbitals produce a large number of closely spaced states. These states of energy are also known as bands of energy.

STRUCTURE OF METALS

In the metals the atoms are packed together in the form of layers to fill the spaces completely as much as possible. This packing is of two types based on the arrangement of the third layer of atoms.

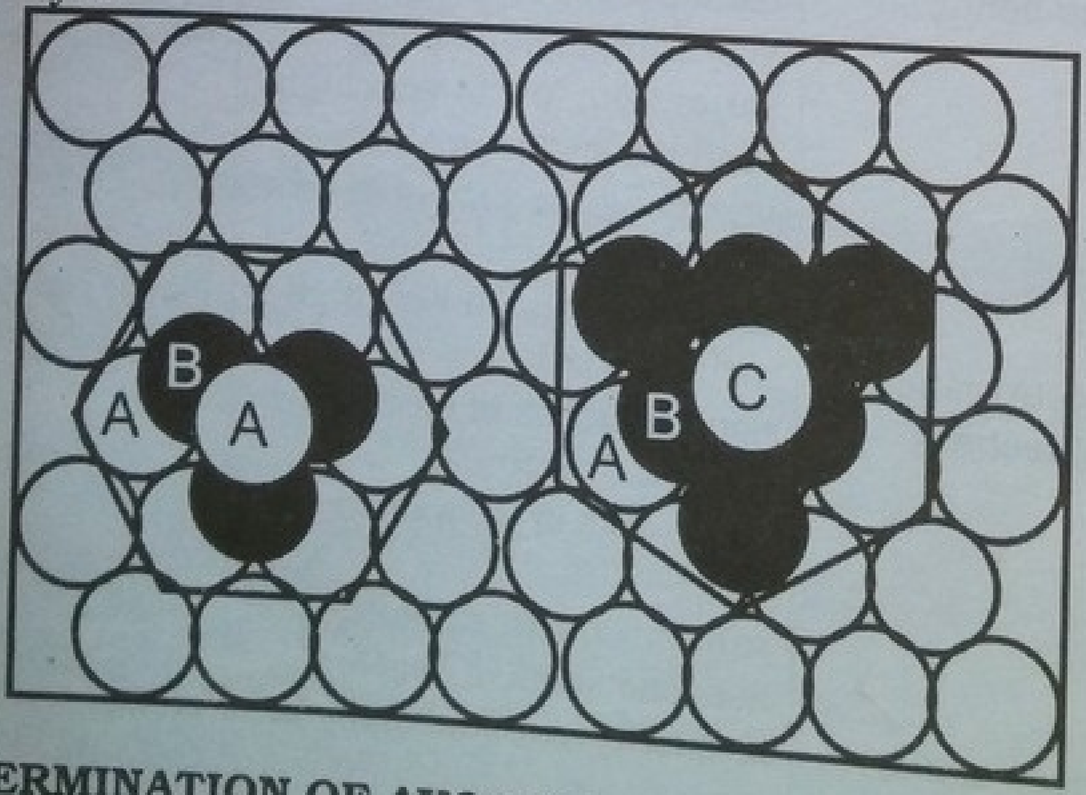
- Hexagonal Close Packing
- Cubic Close Packing

Hexagonal Close Packing
ABAB or 1212

Atom of third layer are over the atoms of second layer as arranged in the first layer.

Cubic Close Packing
ABCABC or 123123

Atoms of third layer are not lying over the atoms of first or second layer.



In ABCABC cubic close packing and ABAB hexagonal close packing the coordination number is 12.

DETERMINATION OF AVOGADRO'S NUMBER (N_A)

Avigadro's number can be calculated in a number of different ways. One of the most accurate methods for determining this number is based on the study of crystalline solids.

The following steps are carried while calculating this number by considering the lithium fluoride. The crystal of LiF is primitive cubic.

- For N_A, we require
  - Molar mass(GFM, GMM, GAM)
  - Density
  - Molar volume
  - Distance among the particles(ions, molecules, atoms)
- Calculate
  - Edge length of crystalline solid(primitive cubic crystal)
  - Number of particles along each edge length
  - Take the cube of the value calculated in the above step.
- Result
  - 6.022×10^{23} particles (ions of one type, molecules, atoms)

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PRACTICE EXERCISE

35 mins
Time Yourself

1. Which of the following has strongest intermolecular forces of attraction?
(a) Hydrogen(H_2) (b) Chlorine (Cl_2)
(c) Iodine (I_2) (d) Methane (CH_4)

2. Which has strongest bonding in the solid state?
(a) Hydrogen Chloride (HCl) (b) Chlorine (Cl_2)
(c) Xenon(Xe) (d) Sodium Chloride (NaCl)

3. When substance moves from a solid to a liquid state, all of the following changes occur except
(a) Molecules become more disordered.
(b) K.E of the molecules decreases
(c) Intermolecular forces become weaker
(d) Molecule become further separated

4. When the atoms of third layer are arranged in such a way that they directly lie above the atoms of first layer then this arrangement is called
(a) ABAB (hexagonal) (b) ABCABC (Cubic)
(c) Orthor hombic (d) Rhombohedral

5. In order to mention the boiling point of water at 110°C, the external pressure should be
(a) Between 760 torr and 1200 torr (b) Between 200 torr and 760 torr
(c) 765 torr (d) any value of pressure

6. Which one is false for evaporation?
(a) Surface phenomenon (b) Continuous
(c) Exothermic (d) Cause cooling

7. Vapour pressure of water at 100°C is
(a) 55 mm Hg (b) 760 mm Hg
(c) 355 mm Hg (d) 1489 mm Hg

8. Which one of the following does not show hydrogen bonding?
(a) Water (b) Ethyl alcohol
(c) Phenol (d) Diethyl ether

9. Liquid crystal is discovered by
(a) William Crooks (b) Fredrick Reinitzer
(c) J.J Thomson (d) Bravis

10. Which one is a conductor but is not malleable?
(a) Iron (b) Graphite
(c) Silver (d) Platinum

11. Hydrogen bonding is involved in
(a) Solubility (b) Cleansing action of detergents
(c) Biological molecules (d) All

12. Actually the vapour pressure on the surface of liquid in the flask is equal to
(a) Δh (b) $Pa - \Delta h$
(c) $Pa + \Delta h$ (d) $Pt = Pa - \Delta h$

13. Forces of attraction, which may be present between all kinds of atoms and molecules are
(a) intramolecular
(b) intermolecular
(c) van der Waal
(d) Dipole-induced dipole

14. The density of water may be
(a) Equal to that of ice
(b) Greater than that of ice
(c) Less than that of ice
(d) All are possible

15. The quantity of heat required to convert one mole of liquid into its vapours at its boiling point is called molar heat of
(a) vaporization
(b) evaporation
(c) crystallization
(d) sublimation

16. Steam causes more severe burn than the boiling water because it possesses.
(a) Latent heat of fusion
(b) Latent heat of vaporization
(c) Latent heat of sublimation
(d) All of the above

17. Water has maximum density at
(a) 0°C
(b) 2°C
(c) 4°C
(d) 100°C

18. The conversion of vapours back into their liquid state is called
(a) crystallization
(b) evaporization
(c) vaporization
(d) condensation

19. Formation of vapours from the surface of a liquid is called
(a) vapourization
(b) evaporation
(c) condensation
(d) cracking

20. When water freezes at 0°C its density decreases due to
(a) Change of bond angles
(b) Cubic structure of ice
(c) Empty space present in the structure of ice
(d) Change of bond length

21. The attractive forces between the partial positive end of one molecule and partial negative end of other molecule are called
(a) Dipole-dipole forces
(b) Ion dipole-dipole forces
(c) London dispersion forces
(d) Debye forces

22. The boiling point increases down the zero group element due to
(a) Ion dipole forces
(b) London forces
(c) Hydrogen bonding
(d) Dipole-dipole forces

23. Vapour pressure is not affected by
(a) Surface area
(b) temperature
(c) intermolecular forces
(d) atmospheric pressure

24. Rising of a wetting liquid in a capillary tube is due to
(a) Surface tension
(b) Cohesive forces
(c) Adhesive forces
(d) viscosity

25. Table salt crystallizes with a
(a) Face centered cubic lattice
(b) body centered cubic lattice
(c) simple cubic lattice
(d) orthorhombic lattice

26. The number of formula units in 29.25g of common salt
(a) $6.022\text{x}10^{23}$
(b) $3.01\text{x}10^{23}$
(c) $2\text{x}N_A$
(d) $4\text{x}6.022\text{x}10^{23}$

27. During which process, empty spaces between particles become minimum?
(a) ionization (b) condensation
(c) fusion (d) evaporation

28. Liquid gets the shape of the container when it is poured into it. Which one of the following reason justifies it?
(a) Liquid do not have definite shape (b) Liquid do not have definite volume
(c) Liquid is highly compressible (d) Liquid molecules can slide over each other

29. Which one of the following has highest volatility
(a) Diethyl ether (b) Ethyl alcohol
(c) Water (d) Ethylene glycol

30. Molar heat of vaporization of water is
(a) 40.7 KJ/mole (b) 40.7 J/mole
(c) 40.7 cal/mole (d) 40.7 Kcal/mole

31. If we provide very high amount of heat to a liquid its boiling point will
(a) increase (b) remains constant
(c) decrease (d) there will be no boiling

32. Crystallites are present in
(a) crystalline solids (b) amorphous solids
(c) liquid crystals (d) all of the above

33. A solid may be made up of
(a) Atoms (b) Ions
(c) Molecules (d) a, b and c

34. A malleable solid is one which can be
(a) Converted into wires (b) Converted into thin sheets
(c) Melted easily (d) All of above

35. Amorphous substances possess
(a) No definite geometry (b) No definite heat of fusion
(c) No sharp melting points (d) All of the above

36. Crystalline solids can be identified easily from their
(a) Sharp melting point (b) Definite geometry
(c) Transition temperature (d) Colour

37. Boiling points of hydrocarbons increase with the increase in number of carbon atoms. It is mainly due to
(a) More strength of H-bonding (b) More strength of London forces
(c) Less polarizability (d) All of the above

38. Ice is ______ crystal
(a) Metallic (b) Molecular
(c) Covalent (d) Ionic

39. Select a pair of compounds, which are isomorphic in nature.
(a) NaCl and KNO_3 (b) MgO and NaF
(c) KNO_3 and MgO (d) NaF and $CaCO_3$

40. The viscosity of solids is
(a) Infinite (b) Negligible
(c) Medium (d) No concept of viscosity in solids

41. $a \neq b \neq c, \alpha \neq \beta \neq \gamma \# 90°$ is representation of crystal system
(a) Monoclinic (b) Triclinic
(c) Hexagonal (d) Trigonal

42. The phenomenon in which a compound exists in two or more crystalline forms is called
(a) Isomorphism (b) Polymorphism
(c) Anisotropy (d) Allotropy

43. Which solids are called true solids?
(a) Metallic (b) Amorphous
(c) Crystalline (d) Vitreous

44. Bucky balls is an allotropic form of
(a) Sulphur (b) Carbon
(c) Silica (d) Tin

45. The number amino acid units for each turn of helix, on average are
(a) 21 (b) 23
(c) 25 (d) 27

46. Isomorphic substances have
(a) Same physical and chemical properties
(b) Same physical and different chemical properties
(c) Different physical and same chemical properties
(d) Different physical and chemical properties

47. If a physical and chemical change takes place at a constant pressure, then the heat change during the process is called
(a) Heat of transition (b) Heat of fusion
(c) Enthalpy change (d) All of above

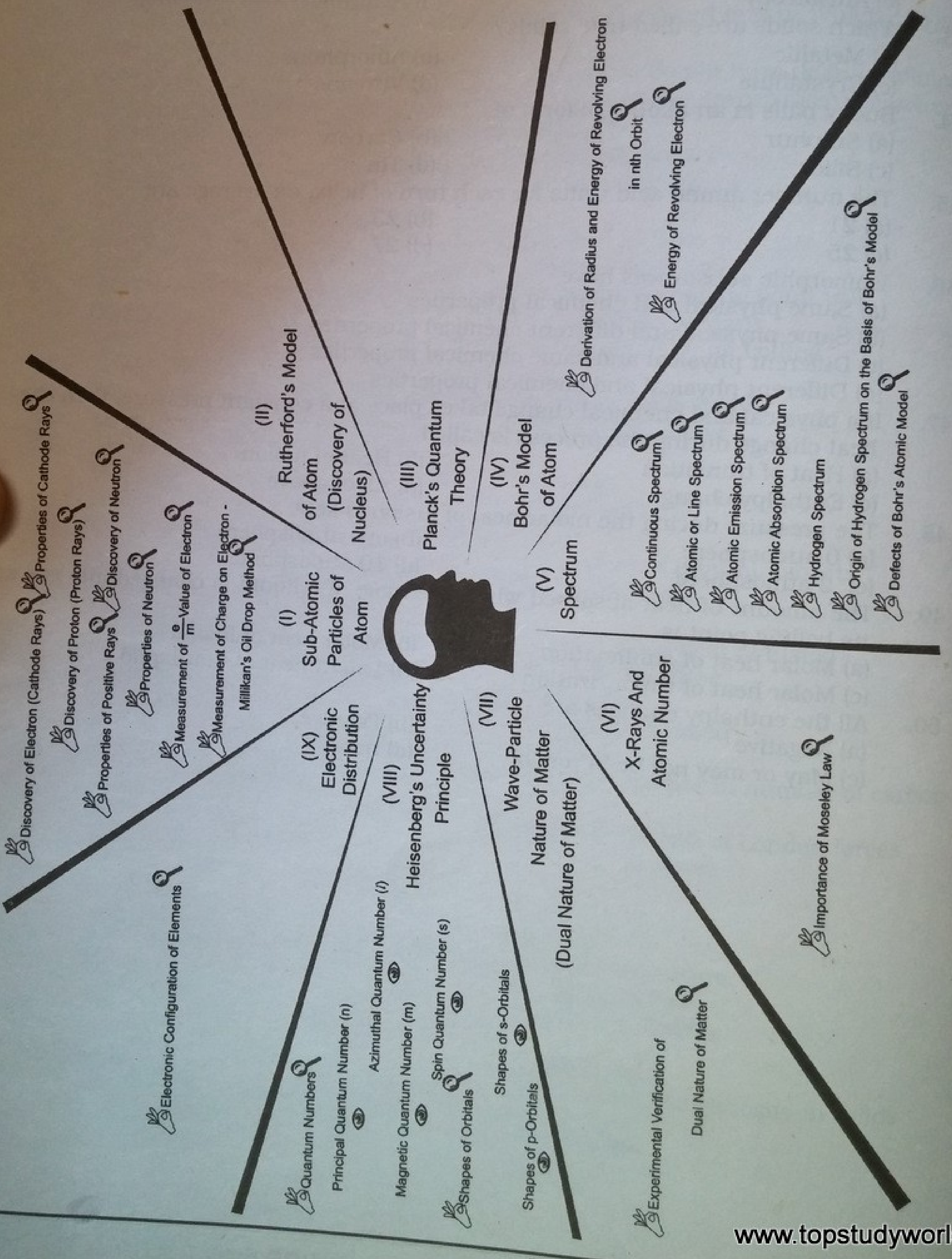
48. The pressure during the molar heat of fusion is kept
(a) 0 atmosphere (b) one atmosphere
(c) 2 atmosphere (d) 10 atmosphere

49. The amount of heat absorbed when one mole of a liquid is changed into gas at its boiling point is
(a) Molar heat of sublimation (b) Molar heat of fusion
(c) Molar heat of vapourization (d) Latent heat of that liquid

50. All the enthalpy changes are
(a) Negative (b) Positive
(c) May or may not be “a” or “b” (d) none

Chapter 5

ATOMIC STRUCTURE


(I) Sub-Atomic Particles of Atom
Discovery of Electron (Cathode Rays)
Properties of Cathode Rays
Discovery of Proton (Proton Rays)
Properties of Positive Rays
Discovery of Neutron
Properties of Neutron
Measurement of $\frac{e}{m}$ Value of Electron
Measurement of Charge on Electron - Millikan's Oil Drop Method
(II) Rutherford's Model of Atom (Discovery of Nucleus)
(III) Planck's Quantum Theory
(IV) Bohr's Model of Atom
Derivation of Radius and Energy of Revolving Electron in nth Orbit
Energy of Revolving Electron
(V) Spectrum
Continuous Spectrum
Atomic or Line Spectrum
Atomic Emission Spectrum
Atomic Absorption Spectrum
Hydrogen Spectrum
Origin of Hydrogen Spectrum on the Basis of Bohr's Model
Defects of Bohr's Atomic Model
(VI) X-Rays And Atomic Number
Importance of Moseley Law
(VII) Wave-Particle Nature of Matter (Dual Nature of Matter)
Experimental Verification of Dual Nature of Matter
(VIII) Heisenberg's Uncertainty Principle
(IX) Electronic Distribution
Electronic Configuration of Elements
Quantum Numbers
Principal Quantum Number (n)
Azimuthal Quantum Number (l)
Magnetic Quantum Number (m)
Spin Quantum Number (s)
Shapes of Orbitals
Shapes of s-Orbitals
Shapes of p-Orbitals

Chapter 5

Atomic Structure

DISCOVERY OF ELECTRON

An English scientist, William Crooks performed discharge tube experiment for the discovery of electron.

Principle

Gases are non-conductor at ordinary pressure. They can be made conductor by decreasing pressure.

Experiment

- A gas is filled in discharge tube
- Strength of voltage depends upon the length of tube and pressure of gas filled.
- At pressure 0.01 torr, rays are produced in discharge tube on applying a potential difference of 5000-10,000 volts.
- Cathode rays are nothing but electrons.

PROPERTIES OF CATHODE RAYS

(a) **Charge**

- In 1895, J.Perrin observed the behavior of cathode rays under the influence of magnetic field.
- In 1897, J.J Thomson noted the negative charge on these rays when passed through electric field.

(b) **Mode of movement**

- These rays cast a sharp shadow of an opaque object placed in their path. They travel perpendicular to the surface of cathode.

(c) **Material particles**

These rays consist of material particles because they possess momentum.

(d) **e/m ratio**

Their e/m ratio is just equal to electrons.

(e) **Penetration power:**

Very low penetration power. However these rays can ionize gases.

(f) **Naming**

Stoney named these particles as electrons.

Do You Know

A television tube works through the deflection of a cathode rays beam by electromagnetic coil.

Do Not Mix

Particle	Symbol
Alpha	$^{4}_{2}He$
Beta	$^{0}_{-1}e$
Neutron	$^{1}_{0}n$
Proton	$^{1}_{1}H$
Neutrino	$^{0}_{0}n$

Points to be remembered

- German physicist, E.Goldstein performed positive rays experiment.
- Positive rays are also called canal rays or anode rays.
- Rutherford suggested a name proton for positive rays particle.
- Chadwick discovered neutron in 1932.
- [Fast neutron] Travel with an energy 1.2Mev
- [Slow neutron] Travel with energy below 1ev

PROPERTIES OF POSITIVE RAYS

Positive Rays
Production They are produced when electric current is passed through gas at low pressure
Charge Have +ve charge as deflected towards -ve pole of electric field.
Move in straight line.
e/m ratio ▪ Smaller than electron ▪ Depends upon the gas filled in tube. ▪ Highest value was obtained when H_2 gas was filled.
▪ Penetration power is very low. ▪ They can ionize gases.
▪ They produce shadow of an opaque object. ▪ They were named canal rays because they travel through perforated cathode electrodes

PROPERTIES OF NEUTRONS

Neutrons
Production They are produced when stream of α-particles are directed at beryllium ($^{9}_{4}Be$).
Charge They are passed undeflected through electric field and magnetic field.
Move in straight line.
▪ Penetration power is very high. ▪ They cannot ionize gases.

MEASUREMENT OF e/m VALUE OF ELECTRON

- Joseph John Thomson calculated the e/m value of electron in 1897.
- Cathode rays are allowed to pass

(i) When both fields (electric and magnetic fields) are off.
(ii) When only magnetic field is applied.
(iii) When only electric field is applied.
(iv) When both fields are applied simultaneously so that canceling the effect of each other and electrons are passed undeflected.
(v) Strengths of the two fields are compared.

- The e/m value of electron is -1.7588×10^{11} C/kg.
- One Kg of electrons have 1.7588×10^{11} Coulombs of charge.

m/e value of electron is 5.686×10^{-12} kg/C

MILLIKAN'S OIL DROP METHOD

An American physicist Robert Millikan determined the charge on an electron.

Mass of Electron	
Method I	**Method II**
e/m= 1.7588×10^{11} C/kg	m/e = 5.686×10^{-12} kg/C
Mass of electron = $\dfrac{1.6022\times10^{-19}C}{1.7588\times10^{11}C/kg}$	Mass of e^- = 5.686×10^{-12} kg/C x 1.6022×10^{-19}C
Mass of electron = 9.1095×10^{-31} kg	Mass of electron = 9.1095×10^{-31} kg

RUTHERFORD'S ATOMIC MODEL

- Rutherford discovered nucleus in 1911.

Experiment

- Bombardment of alpha particles on 0.00004 cm thick gold foil.

Observations

- Rutherford observed the various angle of deflections of alpha particles.
  - ➢ Most of the alpha particles were passed un-deflected.
  - ➢ Some alpha particles were deflected at various angles

Conclusion

- Most of the part of atom is empty.
- Central part is tiny and positively charged. It is called nucleus.
- Almost the whole mass of an atom is concentrated in the nucleus (i.e. atom has non-uniform density).

Objections

If electron is revolving continuously then it will radiate energy continuously then

- Atomic assembly must collapse that doesn't happen.
- Atomic spectrum must be continuous rather than the line spectrum.

AMAZING

If we were to use a golf ball to represent the nucleus, the atom would be about three miles in diameter.

PLANK'S QUANTUM THEORY

In 1900 Plank put forward his theory to explain the emission and absorption of radiations. This theory gives the relationship of energy, frequency, wave length and wave number of photon of light.

- Energy is emitted or absorbed only in terms of wave packets in a discontinuous manner. These wave packets are called quanta or photon.
- Energy of photon or quanta $E \propto \nu$.
- $E = h\upsilon = hc/\lambda = hc\bar{\upsilon}$

Where, h = planks constant = $6.625\text{x}10^{-34}$ Js.

υ = frequency

c = velocity of light = 3×10^{8} m/s

λ = wave length in Å, nm, pm

$\bar{\upsilon}$ = wave number

Important Terminologies

- **Frequency:(ν)**
  Number of waves passing through a point in one second.
- **Wavelength:(λ)**
  The distance between two adjacent crests or troughs.
- **Wave number:($\bar{\nu}$)**
  The number of waves per unit length

BOHR'S ATOMIC MODEL

Postulates

(i) Electron revolves in one of the circular orbits outside the nucleus.

(ii) Electron can revolve only in those orbits in which its angular momentum is integral multiple of unit $h/2\pi$.

$$mvr = nh/2\pi$$

Such orbits are called allowed orbits or stationary state or Bohr's orbits.

(iii) As long as an electron remains revolving in its allowed orbit, the energy of electron remains constant.

(iv) When an electron jumps from higher to lower orbit, it radiates energy in the form of photon of energy as given below.

$$\Delta E = E_2 - E_1 = h\nu$$

Objections

Bohr's Atomic model cannot explain

- The spectrum of poly electron system.
- The fine lines in the atomic spectrum.
- The three-dimensional movement of electrons.
- Zeeman Effect and Stark Effect.

SOMMERFELD'S MODIFICATION OF BOHR'S ATOMIC MODEL

In 1915, Sommerfeld suggested the moving electrons might describe in addition to the circular orbits elliptic orbits as well wherein the nucleus lies at one of the focii of the ellipse.

DERIVATION OF RADIUS OF nth ORBIT

(i) The electrostatic force of attraction between the electron and nucleus is

$$\frac{Ze^2}{4\pi\varepsilon_o r^2}$$

(ii) Centrifugal force balance coulomb's force.

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\varepsilon_o r^2}$$

$$r = \frac{Ze^2}{4\pi\varepsilon_o r^2}$$

on further proceeding, we get;

$$r = \frac{\varepsilon_o n^2 h^2}{\pi m e^2}$$

$$r = a_0\, n^2 (constant)$$

$$a_0 = \frac{\varepsilon_o h^2}{\pi m e^2} = 0.529 A^o$$

By putting the value of n as 1,2,3,4…………, we get

$n_1 = 1$ $r_1 = 0.529A^o$

$n_2 = 2$ $r_2 = 2.11A^o$

$n_3 = 3$ $r_3 = 4.75A^o$

$n_4 = 4$ $r_4 = 8.4A^o$

$n_5 = 5$ $r_5 = 13.22A^o$

Conclusion

(i) The orbits are not equally spaced

$r_2 - r_1, < r_3 - r_2 < r_4 - r_3 < \ldots\ldots\ldots\ldots$

(ii) The second orbit is four times away from the nucleus than first orbit, third orbit is nine times away and similarly fourth orbit is sixteen times away.

ENERGY OF REVOLVING ELECTRON

$$E = E_{\text{kinetic}} + E_{\text{potential}}$$

$$E = \frac{Ze^2}{8\pi\varepsilon_0 r} - \frac{Ze^2}{4\pi\varepsilon_o r}, \; KE = \frac{1}{2}mv^2 = \frac{Ze^2}{8\pi\varepsilon_0 r}$$

Energy of nth orbit

$$E_n = -\frac{me^4}{8\varepsilon_o^2 n^2}\left[\frac{1}{n^2}\right]$$

$$E_n = -2.178\times10^{-18}\left[\frac{1}{n^2}\right] J \text{ per electron}$$

$$E_n = -\frac{1313.315}{n^2}\text{kJmol}^{-1}$$

$$E_1 = -1313.315\text{kJmol}^{-1}$$

$$E_2 = -328.32\text{kJmol}^{-1}$$

$$E_3 = -145.92\text{kJmol}^{-1}$$

$$E_4 = -82.08\text{kJmol}^{-1}$$

$$E_\infty = 0 \text{ kJmol}^{-1}$$

Conclusion

The difference in the values of energy go on decreasing from lower to higher orbits.

$E_2 - E_1 > E_3 - E_2 > E_4 - E_3 > \ldots\ldots\ldots\ldots$

SPECTRUM

A visual display or dispersion of the components of white light, when it is passed through a prism is called a spectrum.

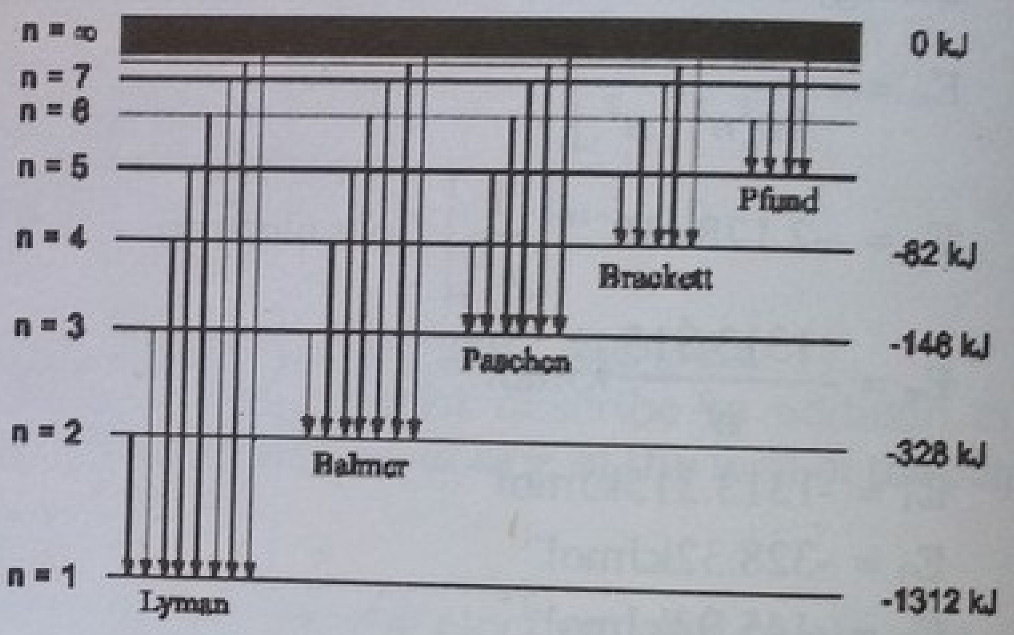
Difference between continuous spectrum and line spectrum

Continuous spectrum	Line spectrum
In this spectrum line or waves are diffused into one another.	In this spectrum lines are separated from each other by some dark spaces.
There is no sharp boundary between the colours.	There is gap between the lines.
It can be formed by dispersing some typical lights like sun light incandescent bulbs light etc.	It is produced by heating the element or its compound on flame or some other source of heat.
It is an effect of polychromatic light	It is an effect of monochromatic light.
Examples: rainbow, sunlight, electric bulb light.	Heating of sodium or potassium or their salts on flame.

Atomic Emission spectra	Atomic Absorption spectra.
It is formed when the substance is in excited state.	It is formed when the substance is in its ground state.
It is produced when the substance reaches the gaseous or vapour state after absorbing energy	It is produced by gases and transparent liquids & solids.
It consists of bright lines present in a dark background.	It consists of black lines present in a bright background.
Emission spectrum of sodium gives two yellow lines of 589.0nm 589.6nm.	Absorption spectrum of sodium gives two dark lines at 589.0nm and 589.6nm.
Origin: When an excited electron jumps from higher to a lower energy level, it emits energy that form colored lines in emission spectra.	Origin: when an electron absorbs energy and moves to higher energy level, dark lines in absorption spectrum indicate the absorbed radiations.

EMISSION SPECTRUM OF HYDROGEN

$n_1=1$;
$n_2=2,3,4,$..............(Lyman series)
$n_1=2$;
$n_2=3,4,5,$...............(Balmer series)
$n_1=3$;
$n_2=4,5,6,$..............(Paschen series)
$n_1=4$;
$n_2=5,6,7,$..............(Brackett series)
$n_1=5$; $n_2=6,7,$.................(Pfund series)

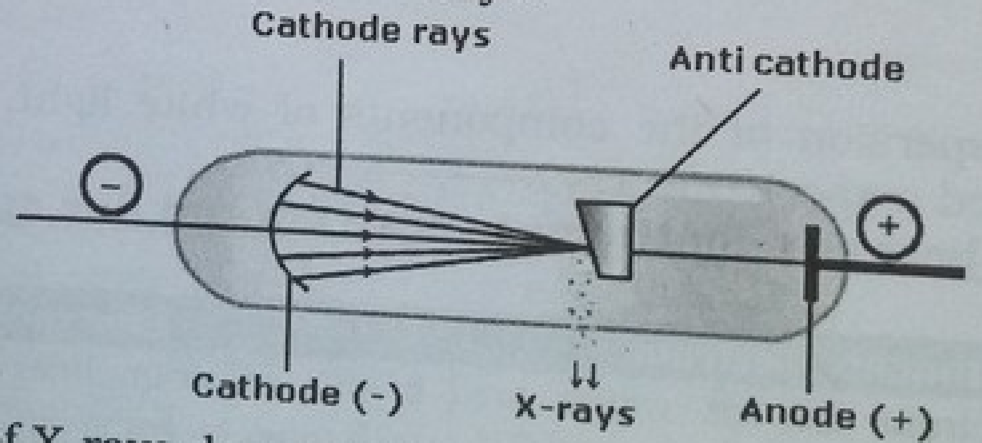


$$\Delta E = 2.18\times10^{-18}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right] J \quad , \quad \bar{v} = 1.0967\times10^{7}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right] m^{-1}.$$

X-RAYS AND ATOMIC NUMBER

Definition

The rays which are produced when rapidly moving electrons collide with heavy metal anode in the discharge tube is called x-rays.



- Wavelength of X-rays depends upon nature of metal.
- Mosley's research work covers the range of wavelength 0.04-8A°.
- Spectral line of shorter wavelength is K-series and of longer wavelength is called L-series.
- X-rays become very short wavelength in case of heavy metals.

Mosley's equation

$$\sqrt{v} = a(z - b)$$

Chapter 5

Atomic Structure

DUAL NATURE OF MATTER

According to de-Broglie "All matter particles (electrons, protons, neutrons, atoms and molecules) possess the characteristics of both the material particle and a wave".

de-BROGLIE'S RELATIONSHIP

$$\lambda = \frac{h}{mv}$$

HEISENBERG'S UNCERTAINTY PRINCIPLE

"It is impossible to determine simultaneously both the position and momentum of an electron with accuracy"

MATHEMATICALLY

$$\Delta x.\Delta P \geq \frac{h}{4\pi}$$

REASON

- The wavelength of visible light is million times larger as compared to diameter of electron. So the position becomes uncertain.
- The x-rays of short wavelength have high energy. So the collision of X-rays with electron will bring about the great uncertainty in momentum.

QUANTUM NUMBERS

The sets of numerical values, which give the acceptable solution to Schrodinger wave equation, are called quantum numbers.

The quantum numbers are:

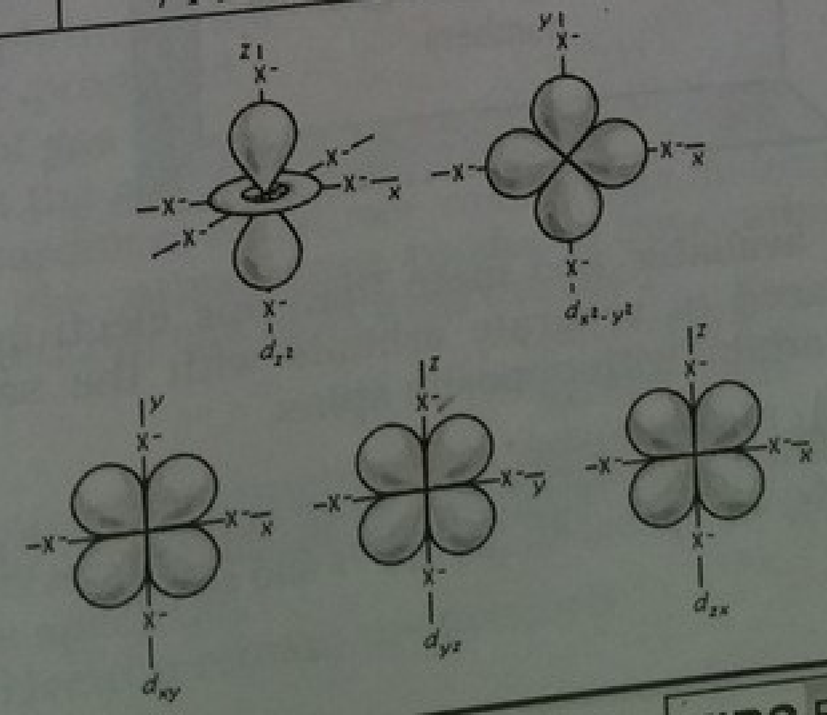
1- Principal quantum number (n)
2- Azimuthal quantum number (ℓ)
3- Magnetic quantum number (m)
4- Spin quantum number (s)

Schrodinger wave equation brings revolution by giving quantum numbers

ORBITAL

The area around the nucleus, where the probability of finding an electron is maximum is called an orbital.

Sub shell	Orbitals	shape
s	1 s-atomic orbital	spherical
p	3 p-atomic orbitals p_x, p_y, p_z	Dumb-bell
d	5 d-atomic orbitals d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$, d_{z^2}	sausage
f	7 f-atomic orbitals	Complex



Arrangement of sub-shells

The sub-shells are arranged in the increasing order of $(n+l)$ value and if any two sub-shells have same $(n+l)$ value, then that sub-shell is placed first whose n value is smaller.

Principal Quantum Number	Azimuthal Quantum Number	Magnetic Quantum Number	Spin Quantum Number	Number of Electrons in Shell
1 K	0 s	0	+1/2, -1/2	2
2 L	0 s 1 p	0 +1, 0, -1	+1/2, -1/2 +1/2, -1/2	2 6 } 8
3 M	0 s 1 p 2 d	0 +1, 0, -1 +2, +1, 0, -1, -2	+1/2, -1/2 +1/2, -1/2 +1/2, -1/2	2 6 } 18 10
4 N	0 s 1 p 2 d 3 f	0 +1, 0, -1 +2, +1, 0, -1, -2 +3, +2, +1, 0, -1, -2, -3	+1/2, -1/2 +1/2, -1/2 +1/2, -1/2 +1/2, -1/2	2 6 } 32 10 14

Electronic Distribution

The following rules are adopted in order to distribute the electrons in the orbitals of sub-shells of shells in an atom.

Auf-Bau's principle

The electrons should be filled in energy sub shells in order of increasing energy values. The electrons are first placed in 1s, 2s, 2p and so on.

Pauli's exclusion principle

Two electrons in the same orbital must have opposite spins.

> It is impossible for two electrons residing in the same orbital of a poly electron atom to have the same values of four quantum numbers

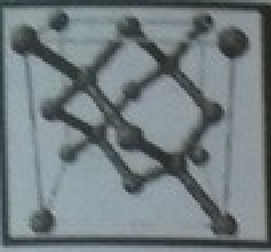
Hunds rule

If degenerate orbitals are available and more than one electrons are to be placed in them, they should be placed in separate orbitals with the same spin rather than putting them in the same orbital with opposite spins.

Note

Half filled and completely filled sub-shells, are more stable e.g. Cr and Cu.

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s and so on.



PRACTICE EXERCISE

35 mins
Time Yourself

1. All of the following were theorized by Bohr in his description of the atom except
   (a) Angular momentum of electrons in multiples of $h/2\pi$
   (b) Electrons revolve in discrete circular orbits.
   (c) Energy of each electron is directly proportional to n^2.
   (d) Electrons radiate energy continuously in a given orbit.
2. The letters s,p,d and f are used to represent which quantum numbers.
   (a) Principal
   (b) Azimuthal
   (c) Magnetic
   (d) Spin
3. The magnetic quantum number (QN) has its values determined directly by the value of
   (a) Principal (QN)
   (b) Azimuthal (QN)
   (c) Spin (QN)
   (d) Both a & b
4. The atomic number of an element having maximum number of unpaired electrons in p-subshell, is
   (a) 7
   (b) 10
   (c) 12
   (d) 16
5. The maximum number of electron in a sub shell with $\ell = 3$ is
   (a) 6
   (b) 10
   (c) 14
   (d) 18
6. Radius of the third shell of H-atom is
   (a) 5.761 A°
   (b) 4.761 A°
   (c) 6.671 A°
   (d) 3.716 A°
7. When an atom absorbs energy the lines in the spectrum will appear which are
   (a) Brighter
   (b) Darker
   (c) Colourless
   (d) Hard to locate
8. Colour of fluorescence produced by cathode rays depends upon
   (a) Temperature
   (b) Pressure
   (c) Volume
   (d) Composition of glass
9. Which one is not true about cathode rays?
   (a) 9.11×10^{-31} Kg
   (b) Cast shadow
   (c) Heat up the platinum foil
   (d) Cannot ionize
10. Positive rays are produced
    (a) By burning of gas
    (b) By cooling of the gas
    (c) By the bombardment of cathode rays on gas molecules
    (d) From anode like cathode rays, produced from cathode
11. A fast moving neutron can eject from nitrogen
    (a) γ -rays
    (b) α -rays
    (c) β -rays
    (d) electrons
12. Rutherford's planet like structure was defective and unsatisfactory because
    (a) Moving e⁻ accelerate towards the nucleus
    (b) Continuous spectrum
    (c) behavior of electron remain unexplained
    (d) All

13. The relationship between energy of a photon of light and its frequency is given by
(a) de-Broglie dual nature of matter
(b) Bohr's model
(c) Planck's Quantum theory
(d) Rutherford's atomic model

14. Splitting of spectral lines when atom is subjected to magnetic field is called
(a) Zeeman's effect
(b) Stark's effect
(c) Photo electric effect
(d) Compton effect

15. The velocity of the photon
(a) Is independent of wavelength
(b) Depends upon source
(c) Depends upon its frequency
(d) Equals to the square of amplitude

16. Which one of the following explain the shape of orbitals?
(a) Principal of quantum number
(b) Azimuthal quantum number
(c) Magnetic quantum number
(d) Spin quantum number

17. Atom cannot be divided into simple units, theorized by
(a) Rutherford
(b) Dalton
(c) Bohr
(d) Schrodinger

18. Pressure in gas discharge tube was kept
(a) 10 torr
(b) 1 torr
(c) 0.1 torr
(d) 0.01 torr

19. The number of fundamental particles in an atom of the lightest isotope of carbon are
(a) 6
(b) 12
(c) 18
(d) 20

20. Angle of deflection was studied by
(a) Hitorff
(b) Stoney
(c) William Crookes
(d) J.Perrin

21. Increase in atomic number is observed during
(a) Alpha emission
(b) Beta emission
(c) Both a & b
(d) Radioactivity

22. Positive rays give flash on
(a) $AgNO_3$ plate
(b) AgCl plate
(c) ZnO
(d) ZnS

23. Free neutron changes into proton with the emission of
(a) Neutrino
(b) Electron
(c) Both a & b
(d) Meson

24. The value of e/m ratio of electron is
(a) 6.02×10^{23} C/kg
(b) 1.7588×10^{20} C/kg
(c) 9.1095×10^{-31} C/kg
(d) 1.7588×10^{11} C/kg

25. Charge of electron was measured by
(a) J.J Thomson
(b) Millikan
(c) Rutherford
(d) Perrin

26. Rutherford bombarded ________ particles in discovery of nucleus.
(a) Gamma-rays
(b) Alpha rays
(c) Beta-rays
(d) X-rays

27. Plank's theory says energy is emitted
(a) In continuous manner
(b) Discontinuous manner
(c) Simultaneously
(d) In the form of heat

28. Angular momentum of an electron
(a) $n^2h/2\pi$
(b) $nh^2/2\pi$
(c) $nh/4\pi$
(d) $nh/2\pi$

29. 2^{nd} orbit is ______ away from nucleus of H-atom as compared to 1^{st} orbit is
(a) 2-times
(b) 3-times
(c) 4-times
(d) 6-times

30. The maximum number of orbitals present in a subshell that is represented by Azimuthal quantum number = 3, will be
(a) 1
(b) 3
(c) 5
(d) 7

31. The correct electronic configuration of Cu is
(a) $[Ar]4s^1$
(b) $[Ar]4s^2$
(c) $[Ar]3d^{10}4s^1$
(d) $[Ar]3d^94s^2$

32. Pfund series are produced in the spectrum of hydrogen atom
(a) when electrons jump down to 2nd- orbit
(b) when electrons jump down to 3rd-orbit
(c) when electrons jump down to 4th-orbit
(d) when electrons jump down to 5th-orbit

33. Atomic orbitals having same energy are called
(a) Degenerate orbitals
(b) Bonding molecular orbitals
(c) Anti bonding molecular orbitals
(d) Half filled orbitals

34. Sommerfeld's modification in Bohr's model is
(a) Orbit is cylindrical
(b) Orbit is elliptical
(c) Orbit is longitudinal
(d) Orbit is asymmetrical

35. When electrons collide with heavy metals, then ______ are produced.
(a) Beta-rays
(b) Alpha-rays
(c) X-rays
(d) Gamma-rays

36. Planck's equation is
(a) $E = mc^2$
(b) $mvr = nh/2\pi$
(c) $E = h\upsilon$
(d) $\lambda = h/mv$

37. Atom with higher atomic number produces X-rays of
(a) Shorter wavelength
(b) Larger wavelength
(c) X-ray not produced
(d) All are possible

38. Wavelength of electron was verified by
(a) Moseley
(b) Davisson and Germer
(c) Einstein
(d) Roentgen

39. Space around nucleus where finding probability of electrons is maximum is called
(a) Orbital
(b) Orbit
(c) subshell
(d) Electron cloud

40. Quantum number which tells the energy of electron, is;
(a) n
(b) l
(c) m
(d) s

41. Electronic configuration of K is
(a) $[Ar]4s^2$
(b) $[Ar]4s^1$
(c) $[Kr]5s^1$
(d) $[He]2s^1$

42. ______ can expel protons from paraffins.
(a) Electron
(b) Positron
(c) Neutron
(d) None of above has such capability

43. Millikan used ______ in his atomizer.
(a) Milk
(b) Honey
(c) Oil
(d) Water

44. Centrifugal forces are balanced in atom by
(a) Attractive forces (b) Repulsive force
(c) Electrons (d) Neutrons

45. Spectrum is produced due to
(a) Different wavelength (b) Different colours
(c) Different intensities (d) all have little contribution

46. When 6d orbital is complete, the entering electron goes into
(a) 7f (b) 7s
(c) 7p (d) 7d

47. When electron jump into orbit 1, then series obtained is
(a) Lyman (b) Paschen
(c) Pfund (d) Brackett

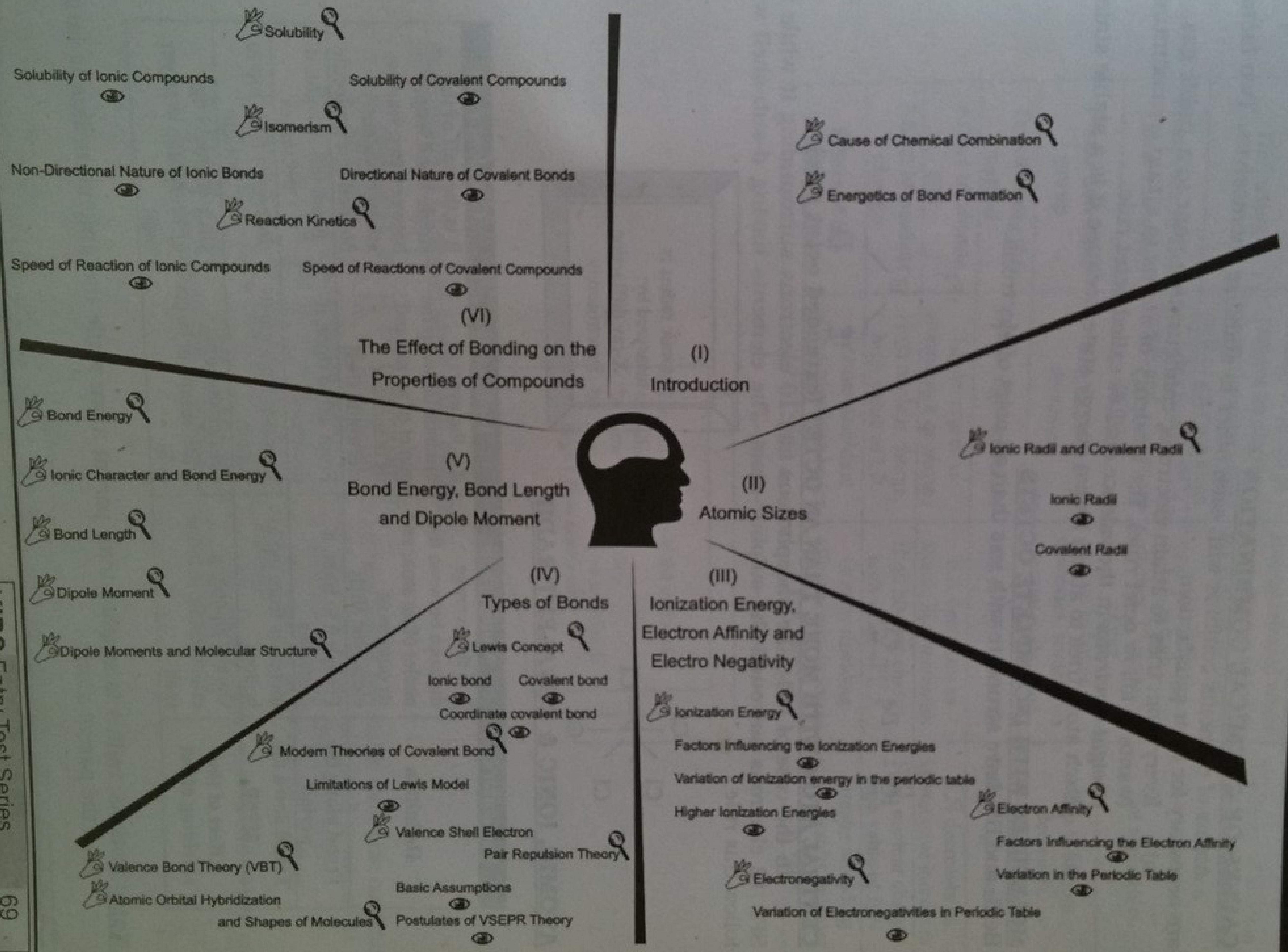
48. Neutrons moving with an energy of 1.2 MeV, are called
(a) Fast neutrons (b) Slow neutrons
(c) Moderate neutrons (d) All are possible

49. Splitting of spectral lines when atoms are subjected to strong electric field is called
(a) Zeeman effect (b) Stark effect
(c) Photoelectric effect (d) Compton effect

50. Three quantum number have been derived from equation of
(a) de-Broglie (b) Planck's
(c) Schrodinger (d) Heisenberg

Chapter 6

CHEMICAL BONDING



(I)
Introduction

- Cause of Chemical Combination
- Energetics of Bond Formation

(II)
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- Ionic Radii and Covalent Radii
  - Ionic Radii
  - Covalent Radii

(III)
Ionization Energy, Electron Affinity and Electro Negativity

- Ionization Energy
  - Factors Influencing the Ionization Energies
  - Variation of Ionization energy in the periodic table
  - Higher Ionization Energies
- Electron Affinity
  - Factors Influencing the Electron Affinity
  - Variation in the Periodic Table
- Electronegativity
  - Variation of Electronegativities in Periodic Table

(IV)
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  - Covalent bond
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- Modern Theories of Covalent Bond
  - Limitations of Lewis Model
- Valence Shell Electron Pair Repulsion Theory
  - Basic Assumptions
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- Atomic Orbital Hybridization and Shapes of Molecules

(V)
Bond Energy, Bond Length and Dipole Moment

- Bond Energy
- Ionic Character and Bond Energy
- Bond Length
- Dipole Moment
- Dipole Moments and Molecular Structure

(VI)
The Effect of Bonding on the Properties of Compounds

- Solubility
  - Solubility of Ionic Compounds
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- Isomerism
  - Non-Directional Nature of Ionic Bonds
  - Directional Nature of Covalent Bonds
- Reaction Kinetics
  - Speed of Reaction of Ionic Compounds
  - Speed of Reactions of Covalent Compounds

Chemical Bond

The force which holds two or more atoms or ions to form a large variety of compounds in called chemical bond.

CAUSES OF CHEMICAL COMBINATION

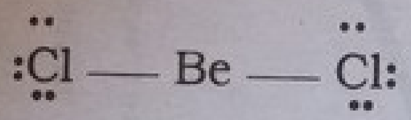
Atoms of elements combine with each other to stabilize themselves. Two factors are necessary for their satisfaction;

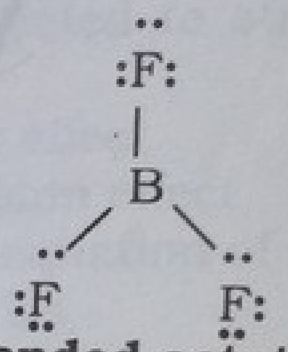
(a) Every atom tries to attain electronic configuration near to a noble gas. (wants to follow octet rule). The tendency of atoms to attain a maximum of eight electrons in the valence shell is called octet rule.

(b) Each atom tries to attain lowest energy state because it is a stable state.

MOLECULES WITH INCOMPLETE OCTETS

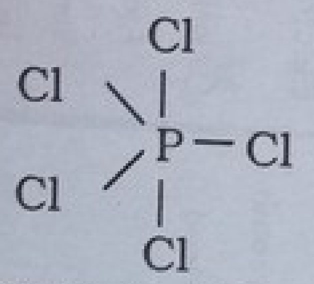
$BeCl_2$ and BF_3 have structure with less than an octet of electrons.





CENTRAL ATOM WITH MORE THAN AN OCTET (extended octet rule)

In the case of PCl_5, the phosphorous has 10 electrons surrounding it while in SF_6, 12 electrons surround the sulphur atom. The elements having d-sub-shell will follow this rule.



Atomic radius is measured by;
- X-ray diffraction
- Spectroscopy

ATOMIC, IONIC & COVALENT RADII

Particulars	Atomic radii	Ionic radii	Covalent radii
Definition	It is the average distance between the nuclei of an atom and its outermost electronic shell	It is the average distance between the nuclei of an ion and its outermost electronic shell	It is the half of the single bond length between two similar atoms covalently bonded in a molecule
Trend along the period	From left to right, it decreases	From left to right, it decreases	From left to right, it decreases
Trend down the group	Increases from top to bottom	Increases from top to bottom	Increases from top to bottom
Effect of the shielding effect	Greater shielding effect results in larger radii	Greater shielding effect results in larger radii	Greater shielding effect results in larger radii

Note: Cationic radius is smaller than parent atom while the anionic radius is larger than the parent atom.

IONIZATION POTENTIAL, ELECTRON AFFINITY & ELECTRONEGATIVITY

Particular	I.P/I.E	E.A	E.N
Definition	Energy required to remove an electron from the outer most shell of gaseous atom	Energy released when an electron is added to the outer most shell of an atom	Tendency of an atom to attract a shared pair of electron
First, second and third energies	1st I.P is lesser, 2nd is higher and 3rd is much higher	1st E.A is high, 2nd is higher, 3rd is much higher	Not applicable
Trend down the group	Top to bottom decreases	Top to bottom decreases; sometimes energy is absorbed	Top to bottom decreases
Trend along the period	Left to right increases	Left to right increases	Left to right increases
Effect of atomic size	I.P decreases as atomic size decreases	E.A decreases as atomic size increases	E.N decreases as atomic size increases
Effect of nuclear charge	High nuclear charge, high value of I.P	High nuclear charge, high value of E.A	High nuclear charge, high value of E.N
Effect of the shielding effect	Greater shielding effect results in lesser I.P value	Greater shielding effect results in lesser E.A value	Greater shielding effect results in lesser E.N value

Ionization energy is the index of Metallic Character
- Low I.E → metals
- Intermediate I.E → metalloids
- High I.E → nonmetals

Exceptional Cases of Ionization energy:

- Among Li, Be, B, Be has maximum I.E
- Among N, O, F, Ne, Ne has maximum I.E because Ne has stable electronic configuration
- Among B,C,N,O, N has maximum I.E because N has half filled p-sub-shell
- Among Ga, In, Tl, Tl has highest I.E because of poor shielding effect
- Among Ca, Sr, Ba, Sr has maximum I.E because poor shielding effect
- Among F, Cl, Cl has more electron affinity
- The element of group IIA, VA, and VIII shows abnormal trend. This can b understood from the distribution of the electrons.

IONIC BOND, COVALENT BOND & CO-ORDINATE COVALENT BOND

Particulars	Ionic bond	Covalent bond	Co-ordinate Covalent bond
Definition	By complete transfer of electrons	By mutual sharing of electrons	By donation of electron pair by one of the bonded atoms
Special	-	▪ Single bond when one electron is shared by each atom ▪ Double bond when 2-electrons are shared by each atom ▪ Triple bond when 3-electrons are shared by each atom	▪ The atom that atom donates an electron pair is called donor ▪ The atom that accepts an electron pair is called acceptor
Types of atoms involved	More electropositive and more electronegative atoms	Usually the atoms of non-metals.	One group, electron deficient; other group electron rich or have lone pair of electrons
E.N difference	Difference more than 1.7	Difference less than 1.7	-
Ionic nature	Complete ionic	Atoms having more E.N will attain δ – charge, while other will get δ +charge	Donor will bear δ+ve charge while accepter will have δ-ve charge
Alignment	It is non- directional.	It is directional.	It is directional.
Representation	It is represented as positive and negative charge e.g. (Na^+Cl^-)	–, =, ≡ **Examples** $H_3C\text{-}CH_3$, $H_2C=CH_2$ $HC\equiv CH$	$\longrightarrow$ **Example** $H_3N{:}\rightarrow BF_3$

Properties Of ionic Compounds & Covalent Compounds

	Properties	Ionic Compounds	Covalent Compounds
1	Conductivity	Conduction of electricity ➢ Non-conductor in solid state. ➢ Conductor in fused or aqueous state.	Non conductor but electrolytes are conductor
2	Thermodynamic properties	High melting point	Low melting point & boiling point
3	Alignment	The bond is non-directional & non-rigid.	The bond is directional & rigid
4	Crystalline properties	Show polymorphism and isomorphism.	Show isomerism
5	Reaction rate	Rate of reaction is high	Rate of reaction is l[illegible]
6	Solubility	Soluble in polar solvents.	Soluble in non-polar solvents

TYPES OF COVALENT BONDS

Non Polar Bond	Polar Bond.
A covalent bond between two similar atoms or those having negligible electronegativity difference.	A covalent bond between two dissimilar atoms having appreciable electronegativity difference but less than 1.7.
The shared pair of electrons is equally attracted by the two bonded nuclei	The shared pair of election is un- equally attracted by the two bonded nuclei.
Electron cloud is symmetrical around the two nuclei.	Electron cloud is unsymmetrical around the two nuclei.
No partial charges appear on the molecule because of symmetrical electrons cloud.	Partial positive and partial negative charges appear because of unsymmetrical electrons cloud.
No polarity is developed on the molecule.	There is polarity in the molecule.
Compounds having non-polar bonds have weak intermolecular attraction.	Compounds having polar bonds have strong intermolecular attraction usually
Compounds having non-polar bond have low boiling point & melting point with less solubility in water.	Compounds having polar bonds have high melting point & boiling point with high solubility in water.
It is a weak bond	It is a strong bond.
Example: H — H	Example: $H^{\delta+} — Cl^{\delta-}$

VALENCE SHELL ELECTRON PAIR REPULSION THEORY
(VSEPR THEORY)

" The valence electron pairs (lone pairs and the bond pairs) are arranged around the central atom to remain at a maximum distance apart to keep repulsion at a minimum."

NOTE
Lone Pair is not involved in determining the shape of the molecules.

The acronym "VSEPR" is pronounced "vesper"

Introduction
- Sidgwick and Powell
- Nylholm and Gillespie

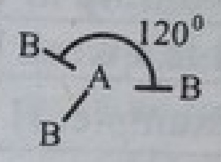
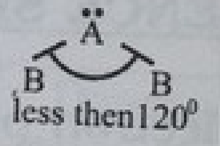
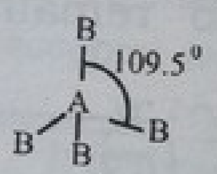
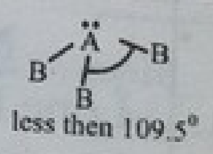
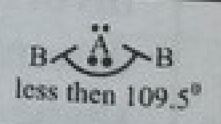
Postulates
- Both lone pair and bond pair determine the geometry of the molecules
- Lone pair occupies more space than a bond pair
- The magnitude of repulsion is in the following order
  Lone pair – Lone pair > Lone pair – Bond pair > Bond pair – Bond pair
- Double bond & triple bond behaves like a single bond in determining the geometry of the molecule.

Ionic > covalent > Metallic > Vander waals forces

Limitations

- VSEPR Theory predicts and explains the shapes of molecules but does not give reasons for the formation of bonds.
- It is not applicable for single bond pair system means di-atomic molecules.
- Complexes do not follow this theory.

CFT & LFT are applied to describe the geometry of complexes

Type	Electron Pairs			Arrangement of pairs	Molecular geometry	Shape	Examples
	Total	Bonding	Lone				
AB_2	2	2	0	Linear	Linear	B–A–B	$BeCl_2$ $HgCl_2$
AB_3	3	3	0	Trigonal planar	Trigonal planar		BH_3,BF_3 $AlCl_3$
		2	1		Bent (or angular)		$SnCl_2$,SO_2
AB_4	4	4	0	Tetrahedral	Tetrahedral		CH_4,$SiCl_4$ CCl_4,BF_4^- NH_4^+,SO_4^{-2}
		3	1		Trigonal pyramidal		NH_3,NF_3 PH_3
		2	2		Bent (or angular)		H_2O, H_2S

Among Alkali earth metals Be form covalent compounds due to high polarizing power.

VALANCE BOND THEORY (VBT)

An approximate theory to explain the bond pair or covalent bond by quantum nechanics.

Basic Theory

According to VBT, a bond between two atoms is formed only when;

1. The two partially filled atomic orbitals should overlap each other.
2. The total number of electrons in both orbitals can never be more than two.

trength

he strength of bond depends on the extent of overlapping. Greater overlapping results a stronger bond.

Sigma bond	Pi bond
A bond formed by linear overlapping of two half filled atomic orbitals of adjacent atoms is called a sigma bond.	A bond formed by the sidewise overlapping of two half filled parallel atomic orbitals of adjacent atoms is called a pi bond.
Electron density is concentrated around the bond axis.	Electron density lies above and below the bond axis.
It has only one lobe of electron density between the nuclei.	It has two lobes of electron density on opposite sides of bond axis.
Only one sigma bond can exist between two atoms.	One or more pi bonds can exist between two atoms.
It offers free rotation about the bond axis	It offers no free rotation about the bond axis.
It has no nodal plane.	It has a nodal plane along the bond axis.
The sigma bonds present in the molecule determine its shape.	Pi bond has no effect on the shape of the molecule.

FORMATION OF SOME IMPORTANT COMPOUNDS

Particulars	H_2 molecule	H_2O molecule	NH_3 molecule
Atomic orbital participating	1s will take part	1s of H and $2p_y$, $2p_z$ of O will take part	$2p_x$, $2p_y$, $2p_z$ of N and 1s of H will take part
Nature of bond	Sigma bond	Sigma bond	Sigma bond
Angle of bond	No	104.5°	107.5°
Number of lone pair of electrons	No	Two lone pairs at O atom	One lone pair at nitrogen atom

HYBRIDIZATION

A process in which atomic orbitals of different energies and shapes are mixed together to form a new set of equivalent orbitals of the same energy and same shape is called hybridization

- Hybridization is a process of mixing of orbitals in a single atom (or ion).
- Only orbitals of comparable (relatively close) energies can be mixed to form hybrid orbitals.
- The number of hybrid orbitals is always equal to the number of orbitals which are mixed.
- Once an orbital has been used to form hybrid orbitals, it is no longer available for the electrons.

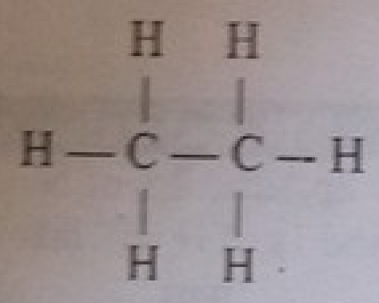
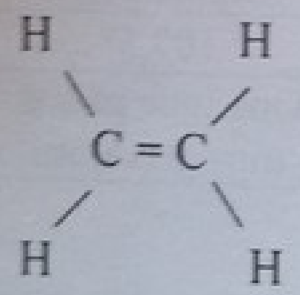
Hybrid atomic orbitals

The atomic orbitals of same energy, which have been formed due to mixing of different orbitals of different energies, are called the hybrid atomic orbitals.

Types Of Hybridization In Hydrocarbons

Particular	sp^3	sp^2	sp
Definition	Mixing of one-s and three p-atomic orbitals	Mixing of one-s and two p-atomic orbitals	Mixing of one-s and one p-atomic orbitals
Geometry	Tetrahedral	Trigonal planar	Linear
Nature of bonds	4 σ-bonds	3 σ-bonds, 1π-bond	2 σ-bond and 2 Π-bonds

STRUCTURE OF HYDROCARBONS ON BASIS OF HYBRIDIZATION

Structure	Number of bonds	Hybridization	Bond angle	Sigma bonds	Pi bonds
	7	sp^3	109.5^0	7	0
	6	sp^2	120^0	5	1
$H-C\equiv C-H$	5	sp	180^0	3	2

MOLECULAR ORBITAL THEORY (MOT)

- The molecular orbital approach considers the whole molecule as a single unit. A molecular orbital describes a region of space in a molecule where electrons are most likely to be found, and it has a specific size, shape and energy level.
- Molecular orbitals are formed by overlapping the atomic orbitals of combining atoms. The number of molecular orbitals formed is the same as the number of atomic orbitals overlapped.
- Molecular orbitals that are lower in energy than the atomic orbitals are bonding; MOs that are higher in energy than the atomic orbitals are anti bonding MOs.
- Electrons are filled in molecular orbitals starting from of lowest energy MOs. Only two electrons can occupy each orbital, with opposite spin (paired spin).
- Bond order can be calculated by subtracting the number of electrons in bonding MOs divided by number of electrons in anti bonding MOs.

Atomic Orbital

A wave function whose square gives the probability of finding an electron within a given region of space in an atom.

Molecular Orbital

A wave function whose square gives the probability of finding an electron within a given region of space in a molecule.

Molecular Orbital theory

The molecular orbital theory considers the whole molecule as a single unit.

Atomic Orbital	Molecular Orbital
An orbital that surrounds only one nucleus is called an atomic orbital.	An orbital that surrounds more than one nuclei is called molecular orbital.
An atomic orbital is always associated with a single atom	A molecular orbital is associated with two or more atoms.
Atomic orbital has a definite size and shape.	The shape of a molecular orbital depends on the shape of the atomic orbital forming it.
An atomic orbital is associated with a definite amount of energy.	A molecular orbital has lower or higher energy than the total energy of atomic orbitals forming it.
Electron present in AO is influenced by only one nucleus.	Electron present in MO is influenced by two nuclei.

DIFFERENCE BETWEEN BMO AND ABMO

Bonding Molecular Orbital	Anti-bonding Molecular Orbital
A molecular orbital that has lower energy than the atomic orbitals from which it is formed is called a bonding molecular orbital.	A molecular orbital that has higher energy than the atomic orbitals from which it is formed is called an antibonding molecular orbital.
Most of the electron density lies between the nuclei of the two bonded atoms.	Most of the electron density lies away from the space between the nuclei of the bonded atoms.
Electrons in bonding orbital are responsible for attraction	Electrons in an antibonding orbital are responsible for repulsion

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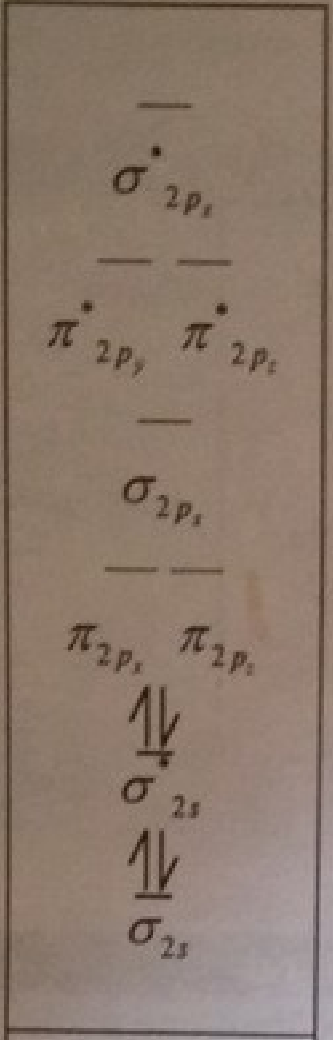
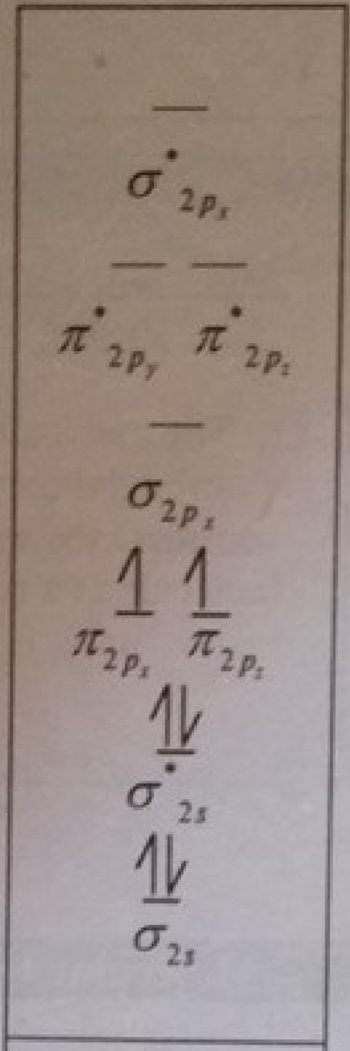
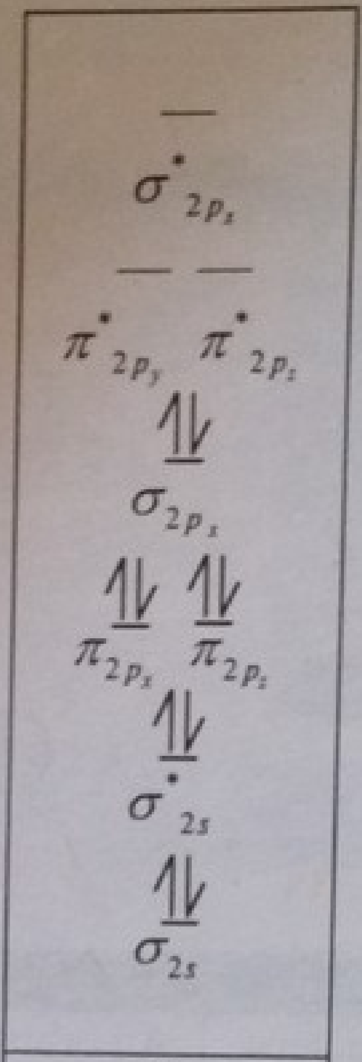
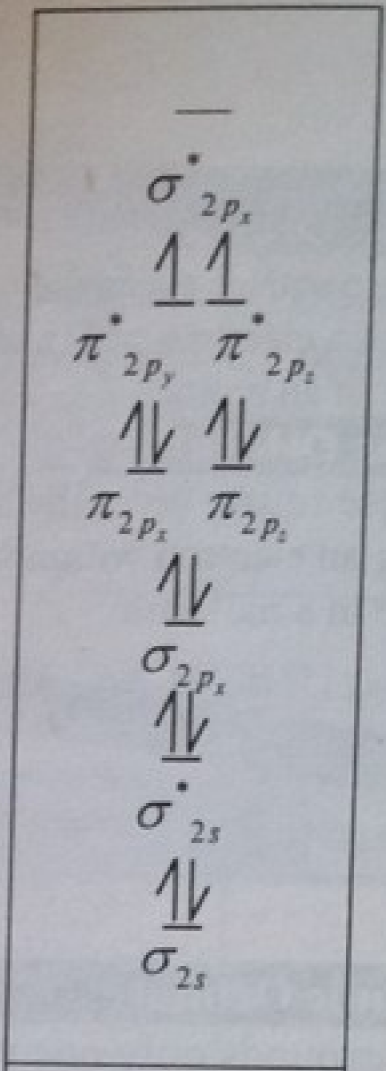
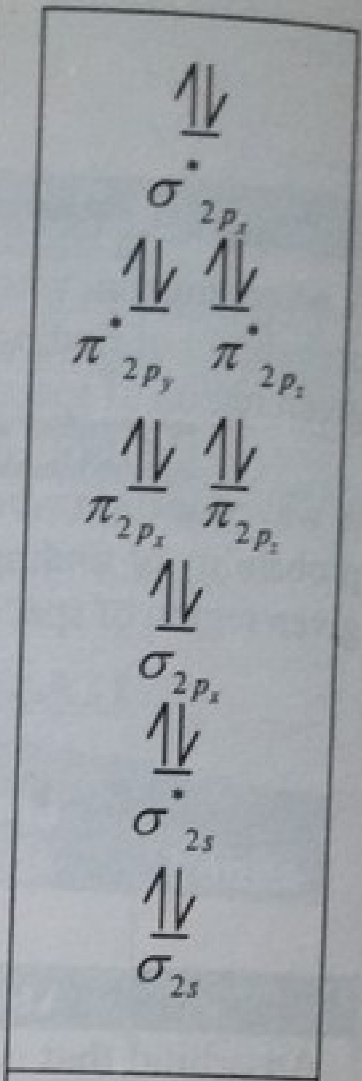
 $\sigma^*_{2p_x}$ $\pi^*_{2p_y}$ $\pi^*_{2p_z}$ σ_{2p_x} π_{2p_y} π_{2p_z} σ^*_{2s} σ_{2s}	 $\sigma^*_{2p_x}$ $\pi^*_{2p_y}$ $\pi^*_{2p_z}$ σ_{2p_x} π_{2p_y} π_{2p_z} σ^*_{2s} σ_{2s}	 $\sigma^*_{2p_x}$ $\pi^*_{2p_y}$ $\pi^*_{2p_z}$ σ_{2p_x} π_{2p_y} π_{2p_z} σ^*_{2s} σ_{2s}	 $\sigma^*_{2p_x}$ $\pi^*_{2p_y}$ $\pi^*_{2p_z}$ π_{2p_y} π_{2p_z} σ_{2p_x} σ^*_{2s} σ_{2s}	 $\sigma^*_{2p_x}$ $\pi^*_{2p_y}$ $\pi^*_{2p_z}$ π_{2p_y} π_{2p_z} σ_{2p_x} σ^*_{2s} σ_{2s}
Be_2	B_2	N_2	O_2	Ne_2
Bond order $2-2=0$	Bond Order $\frac{4-2}{2}=1$	Bond Order $\frac{8-2}{2}=3$	Bond Order $\frac{8-4}{2}=2$	Bond Order $8-8=0$
Bonds = 0	Bonds = 1	Bonds = 3	Bonds = 2	Bonds = 0

BOND ENERGY

The average amount of energy required to break all bonds of a particular type in one mole of the substance is called bond energy.

- Unit of bond energy is kJ/mole.

Factors Effecting Bond Energy

The bond energy is the measure of the strength of bond. The strength of a bond depends upon the following factors.

1- Electronegativity difference of bonded atoms
2- Sizes of the atoms
3- Bond length

BOND LENGTH

The distance between the nuclei of two atoms forming a covalent bond is called bond length.

- Techniques used to determine bond length are electron diffraction, X-ray diffraction or spectral studies.
- Greater the E.N difference between bonded atoms, shorter will be bond length.
- Ionic character shortens bond length.
- Greater the atomic radii of the bonded atoms larger will be the bond length.
- Involvement of π-bond reduces bond length.
- Greater s-character in the hybrid orbital results in shorting of bond length.
- Along the period, bond length decreases.

- Down the group, bond length increases.

Compound	Bond	Bond length (pm)
BF_3 (sp^2 hybridized)	B-F	130
BCl_3 (sp^2 hybridized)	B-Cl	175
SiH_4 (sp^3 hybridized)	Si-H	148
SiF_4 (sp^3 hybridized)	SI-F	155
C_2H_6 (sp^3 hybridized)	C-C	154
C_2H_4 (sp^2 hybridized)	C=C	133
C_2H_2 (sp hybridized)	C ≡ C	120
$(CH_3)_2C=O$ (sp^2 hybridized)	C=O	122

Applications of bond energy

- Relative strength of bonds
- % of ionic character in bond
- Estimation of ΔH

DIPOLE MOMENT

The product of the electric charge and the distance between the positive and negative centers is called dipole moment. Dipole moment is a vector quantity. Mathematically, it can be written as;

$$\mu = q \times r$$

Units

(i) Coulomb metre (Cm)
(ii) Debye (D)

$$1D = 3.336 \times 10^{-30} Cm$$

Applications

- % of ionic character
- Geometry of molecules

RELATION BETWEEN MOLECULAR GEOMETRY AND DIPOLE MOMENT

Formula	Molecular Geometry	Dipole Moment
Ax	Linear	Can be non zero
AX_2	Linear Bent	Zero Can be non zero
AX_3	Trigonal planar Trigonal pyramidal T-shaped	Zero Can be non zero Can be non zero
AX_4	Tetrahedral Square planar Seesaw	Zero Zero Can be non zero
AX_5	Trigonal bipyramidal Square pyramidal	Zero Can be non zero
AX_6	Octahedral	Zero

PRACTICE EXERCISE

35 mins Time Yourself

1. The relative attraction of the nucleus for the electrons in a chemical bond is called
(a) Ionization energy
(b) Electron affinity
(c) Electro negativity.
(d) None of the above

2. The ionization energy
(a) Generally increases from left to right in a period.
(b) Does not change in a period
(c) Increase from top to bottom in a group
(d) Does not change in a group

3. Which of the following will have highest value of electron affinity
(a) F
(b) Cl
(c) Br
(d) I

4. Which type of bond is formed by overlap of p orbitals
(a) Pi(π)
(b) Sigma(σ)
(c) Both.
(d) Neither

5. The octet rule does not always hold for which of the following elements?
(a) C
(b) O
(c) F
(d) P

6. Which of the solid does not contain covalent bond
(a) Copper.
(b) Ice
(c) Diamond
(d) Graphite

7. Which of the following is the best explanation that CO_2 is non polar molecule
(a) Linear geometry
(b) Dipole moment is zero
(c) Sp hybridization
(d) None

8. Shielding effect across the period
(a) Increases
(b) Decreases
[✓ (c) Constant]
(d) None

9. Which one is not the absolute term of the element?
(a) Ionization energy
(b) Electron affinity
(c) Electro negativity
(d) Atomic size.

10. Which one has maximum number of unpaired electrons?
(a) $_6X$
(b) $_7Y$.
[✓ (c) $_9Z$]
(d) $_{13}W$

11. The molecule having π-bond
(a) H_2O
(b) C_2H_6 Ethane
[✓ (c) O_2]
(d) NH_3

12. When 2 lone pair and 2 bond pair are around the central atom, reduction in the bond angle is up to.
(a) 109.5°
(b) 104.5°.
(c) 107.5°
(d) 102°

13. In O_2, each oxygen atom is hybridized
(a) sp^3
[✓ (b) sp^2]
(c) sp
(d) All

14. Molecular orbitals are filled according to
(a) Auf bau principle
(b) Hund's rule
(c) Pauli's Exclusion principle
[✓ (d) All these]

15. Measurement of the degree of polarity is
(a) Electron affinity
(b) Ionic character
(c) Ionization energy
[✓ (d) Dipole moment]

16. Which one shows high %age of the ionic character?
(a) H_2O
[✓ (b) HF]
(c) HCl
(d) HBr

17. A specie with maximum number of unpaired electrons.
(a) F^-
(b) H_2O
(c) HF
[✓ (d) NH_2^-]

18. Which of the following have their outer most shell complete in atomic form?
[✓ (a) Noble gases]
(b) Alkali metals
(c) Coinage metals
(d) Gun metals

19. Force responsible to hold atoms together in a compound is called
[✓ (a) Bond]
(b) Attractive force
(c) Interaction
[✓ (d) All of above represent same entity]

20. Energy of atom in compound is
[✓ (a) Higher than individual]
[✓ (b) Lesser than individual]
(c) No change
(d) Impossible to predict

21. In a period, the atomic radii
(a) Increases
[✓ (b) Decreases]
(c) Remain same
(d) First decreases, then increases

22. An atom loses or gains electrons, to
(a) Gain stability
(b) Form a bond
(c) Complete its outermost shell
[✓ (d) All are accurate justifications.]

23. In a group, ionic radii
[✓ (a) Increases]
[✓ (b) Decreases]
(c) No change
(d) Variable trend

24. Energy required to remove electron from an atom
[✓ (a) Ionization potential]
(b) Electronegativity
(c) Electron affinity
(d) Activation energy

25. Ionization energy in a period generally
[✓ (a) Increases]
(b) Decreases
(c) No change
(d) Variable trend

26. Greater shielding effect corresponds to ionization energy value
(a) Greater
[✓ (b) Lesser]
(c) Remain same
(d) No effect

27. Elements having high I.P values are
(a) Metals
[✓ (b) Non metals]
(c) Liquids
(d) Solids

28. Energy released or absorbed when electrons are added in atom is
(a) Ionization potential
(b) Electronegativity
[✓ (c) Electron affinity]
(d) Activation energy

29. In a period, electronegativity from left to right
[✓ (a) Increases]
(b) Decreases
(c)Remain constant
(d) Variable trend

30. Ionic bond is produced after complete transfer of
(a) Nucleus
(b) Neutrons
(c) Electrons
(d) Protons

31. Elements of group IA, IIA are
(a) Electronegative
(b) Electropositive ✓
(c) Neutral
(d) IA is electropositive, while IIA is electronegative

32. Bond will be ionic, when E.N difference of bonded atom is
(a) Equal to 1.7
(b) Greater than 1.7
(c) Less than 1.7
(d) No specificity exists

33. Mostly ionic compound are produced in between elements of
(a) IA and VIA
(b) IA, IIA and VIIA
(c) IB and VIIB
(d) IA and IB

34. Which one of the following has polar covalent bond?
(a) HF
(b) CH_4
(c) H_2
(d) N_2

35. The Lewis acids are
(a) Electron deficient
(b) Electron rich
(c) Octet is complete
(d) No such acids exist

6. Sharing of 1 electron pair by one specie forms
(a) Single covalent bond
(b) Hydrogen bond
(c) Double covalent bond
(d) Coordinate covalent bond

37. Angle in water molecule is
(a) 104.9°
(b) 104.5°
(c) 109.5°
(d) 120°

38. The geometry of ammonia is
(a) Tetrahedral
(b) Square planner
(c) Trigonal bipyramidal
(d) Trigonal Pyramidal

39. Orbitals of same energy produced after mixing of orbitals of different energy are called
(a) Degenerate orbitals ✓
(b) Generate orbitals
(c) Hybrid orbitals
(d) Zeeman orbitals

40. By combining "n" atomic orbitals, no. of hybrid orbitals will be
(a) 2n
(b) n
(c) 3n
(d) impossible to predict

41. In sp^3 hybridization
(a) All p-orbitals are involved
(b) One s and 3 p-orbitals are involved
(c) one p-orbital is involved
(d) four p-orbitals are involved

42. Geometry of simple molecule having sp^3 hybrid orbital is
(a) Triangular
(b) Tetrahedral
(c) Square planner
(d) Linear

43. Geometry of molecule will be pyramidal, if the outer most shell of the central atom has
(a) 3 bond pair, one lone pair
(b) 2 bond pair, 2 lone pair
(c)1 bond pair, 3 lone pair
(d) 3 lone pair, 1 bond pair

44. Pi bonds are produced by overlapping of
(a) Un-hybrid orbitals ✓
(b) Hybrid orbitals
(c) Hybrid and un hybrid orbitals
(d) atomic orbital and hybrid orbital

45. According to VESPR Model, the geometry of molecule having 5 bond pair in outer most shell will be
(a) Triangular
(b) Square planner
[✓ (c) Trigonal bipyramidal]
(d) Octahedral

46. Molecular orbital, which have higher energy than atomic orbitals is called
(a) Bonding molecular orbital
[✓ (b) Antibonding molecular orbital]
(c) Hybrid orbital
(d) Super atomic orbital

47. Unpaired electron in a molecule gives _______ character.
(a) Ferromagnetic
[✓ (b) Paramagnetic]
(c) Diamagnetism
(d) Both a & b

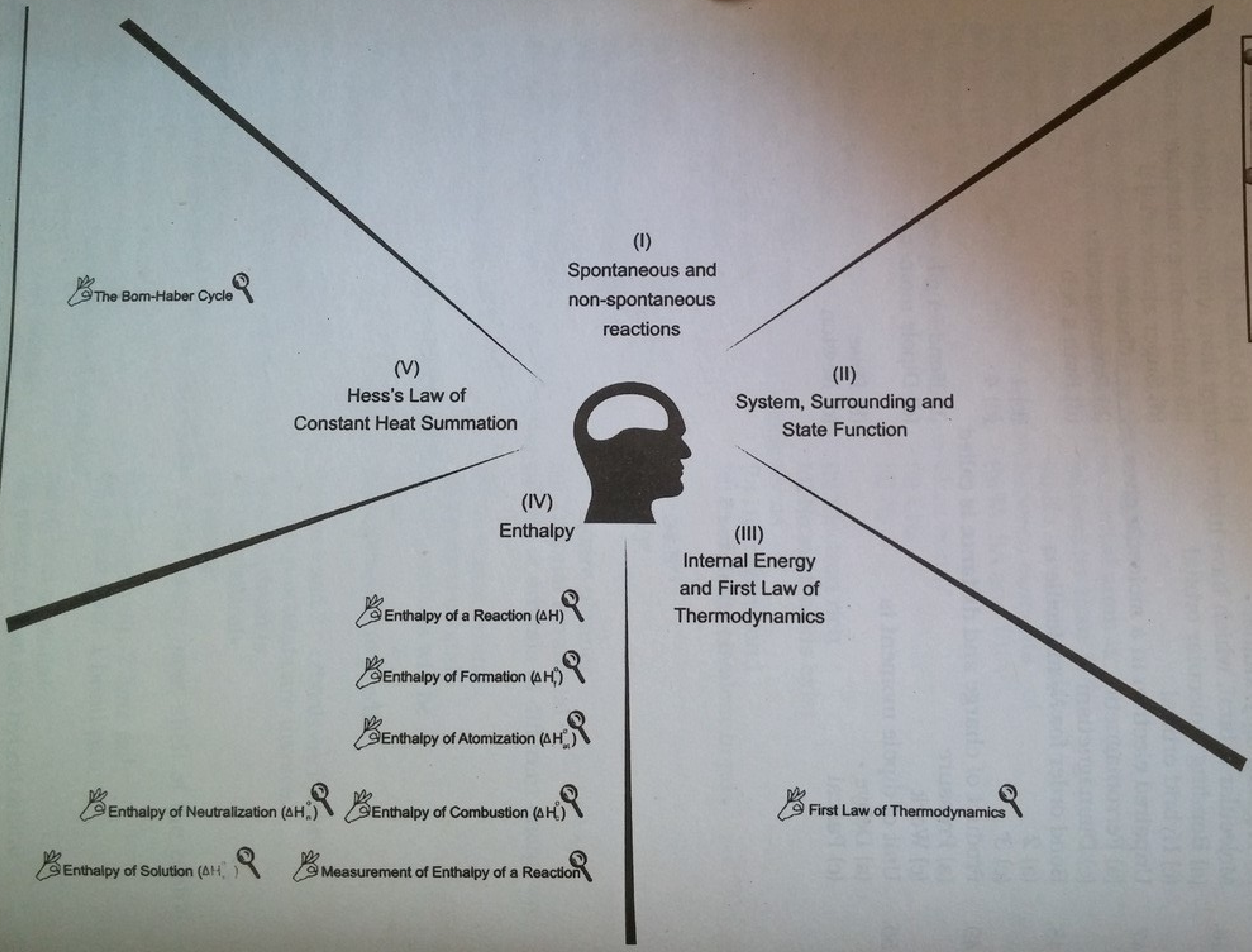
48. Bond order for N_2 molecule is
(a) 2
(b) 1
[✓ (c) 3]
(d) 4

49. Product of charge and distance is called
(a) Pressure
(b) Bond length
(c) Work
[✓ (d) Dipole moment]

50. Unit of dipole moment is
[✓ (a) Debye]
(b) Poise
(c) Pascal
(d) Newton

Chapter 7

THERMOCHEMISTRY



(I) Spontaneous and non-spontaneous reactions

(II) System, Surrounding and State Function

(III) Internal Energy and First Law of Thermodynamics

- First Law of Thermodynamics

(IV) Enthalpy

- Enthalpy of a Reaction (ΔH)
- Enthalpy of Formation (ΔH_f°)
- Enthalpy of Atomization (ΔH_{at}°)
- Enthalpy of Combustion (ΔH_c°)
- Enthalpy of Neutralization (ΔH_n°)
- Measurement of Enthalpy of a Reaction
- Enthalpy of Solution (ΔH_{sol}°)

(V) Hess's Law of Constant Heat Summation

- The Born-Haber Cycle

Chapter 7

Thermochemistry

THERMOCHEMISTRY

The study of heat changes during a chemical reaction is called thermochemistry.

ENERGY

"Ability of a body to do work is called energy."

TYPES OF ENERGIES

(i) Kinetic energy (K.E)→Energy due to motion
(ii) Potential energy (P.E)→Energy due to position, shape and orientation
(iii) Sound energy
(iv) Heat energy
(v) Magnetic energy
(vi) Mechanical energy
(vii) Solar energy

UNITS OF ENERGY

Units	Relation
Joule (SI Unit)	$J=kgm^2s^{-2}$
British thermal unit	$1B.T.U=1.055 \times 10^3 J$
Kilo watt hour	$1Kwh = 3.6 \times 10^6 J$
Calorie	1 Cal = 4.184J
erg	$1J=10^7 ergs$

SYSTEM

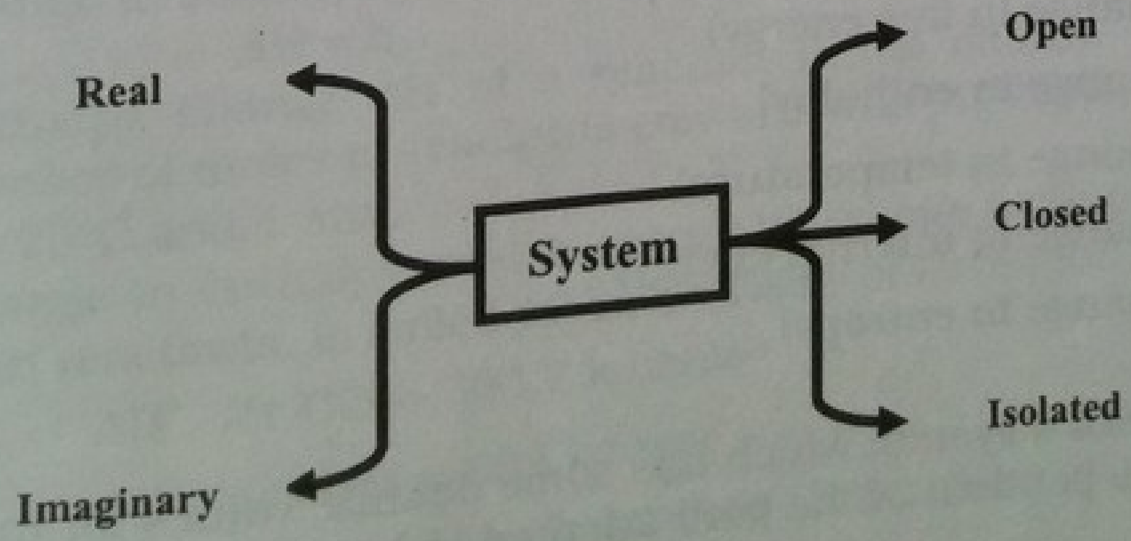
"The portion of universe which is set aside for consideration, observation, discussion, argumentation or experimentation is called system"

OR

"The substance under consideration is called chemical system"

Examples

(i) $Pb(NO_3)_2$ under consideration is a system.
(ii) The liquid whose boiling point is to be measured is a system.



SURROUNDING

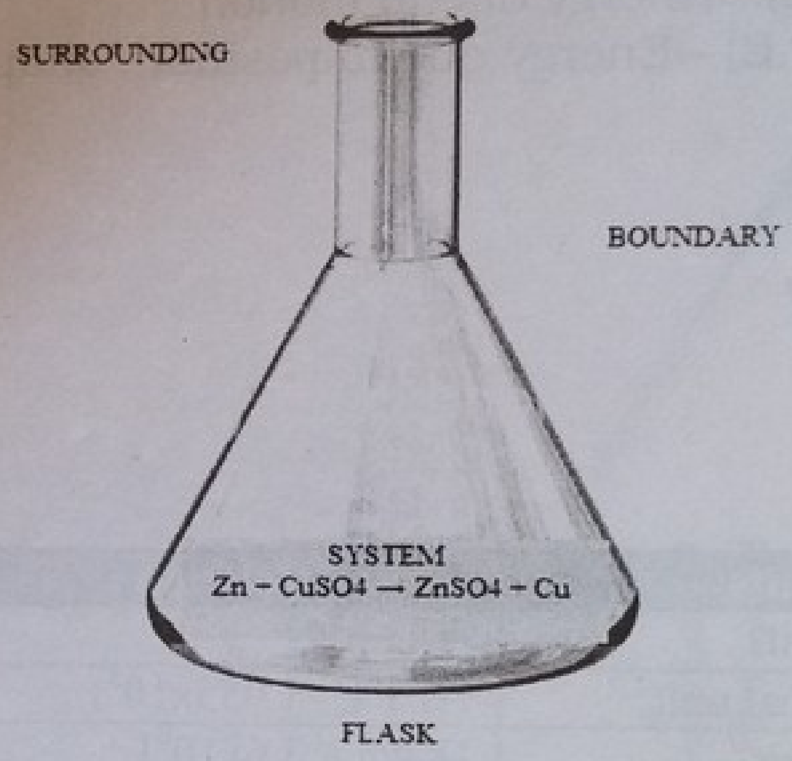
The portion of universe except system is called surrounding.

Example

A chemical reaction happening in a test tube is a system, while the walls of the test tube and the atmosphere are its surrounding.

BOUNDARY

The real or imaginary surface, separating the system from surrounding is called boundary of a system.



STATE

The condition of a system is called state of the system.

EXAMPLES

Volume, Temperature, Pressure, Energy etc

	State	Examples
1	Conditions describing the system before it undergoes a change are called initial states of system.	V_1, T_1, P_1, E_1
2	Conditions describing the system after it undergoes a change are called final states of system.	V_2, T_2, P_2, E_2

CHANGE IN THE STATE OF SYSTEM

$\Delta V = V_2 - V_1$ (Change in volume)

$\Delta P = P_2 - P_1$ (Change in pressure)

$\Delta G = G_2 - G_1$ (Change in free energy)

$\Delta H = H_2 - H_1$ (Change in enthalpy)

$\Delta T = T_2 - T_1$ (Change in temperature)

$\Delta E = E_2 - E_1$ (Change in internal energy)

$\Delta S = S_2 - S_1$ (Change in entropy)

STATE FUNCTION

A macroscopic property of a system which has some definite values for initial and final states, and which is independent of the path adopted to bring about a change.

Examples

Pressure (P), Temperature (T), Volume (V), Internal energy (E) and enthalpy (H) are all state functions.

- Capital symbols are used for state function.
- Heat and work are not state functions.
- Internal energy E is a state function.

INTERNAL ENERGY

"The sum of potential energy and kinetic energy of a substance is called its internal energy."

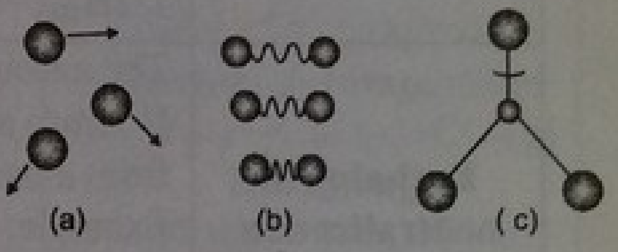
OR

"The sum of all the possible kinds of energies of a system is called its internal energy (E)."

$$E_T = K.E + P.E + \ldots\ldots\ldots$$

Internal energy

- **Kinetic energy**
  - ➢ Translational kinetic energy (a) (mono-atomic)
  - ➢ Rotational kinetic energy (c) (tetra-atomic)
  - ➢ Vibrational kinetic energy (b) (di-atomic)
- **Potential energy**
  - ➢ Intra-molecular forces
  - ➢ Inter-molecular forces
- **Effect of increase in Internal Energy:**
  - i) The temperature of the system may increase
  - ii) A phase change may occur.
  - iii) A chemical reaction may take place.



FIRST LAW OF THERMODYNAMICS (LAW OF CONSERVATION OF ENERGY)

"Energy can neither be created nor be destroyed, but can be changed from one form to another."

$$\Delta E = q + P\Delta V$$

$$\Delta E = q_v$$

ENTHALPY

The total heat content of a system is called enthalpy of a system.

- It is a state function.
- In a given state, enthalpy cannot be calculated.
- Change in enthalpy is equal to heat of reaction at constant pressure

  $$\Delta H = q_P$$
- Enthalpy change ΔH of a reaction is the change that occurs when certain number of moles of reactants converts into products under standard conditions i.e. 25°C and 1 atm.
- Change in enthalpy, which occurs when one mole of a compound is produced from reactants, is called molar enthalpy of formation (ΔH_f).

  e.g. ΔH°_f for $CO_2 = -393.7\ kJmole^{-1}$

  ΔH°_f for $MgO = -692\ kJmole^{-1}$
- Standard enthalpy of a substance is chosen 'zero'.
- $q_P > q_v$ or $\Delta H > \Delta E$

Enthalpy	Definition	Symbol
Enthalpy of reaction	The enthalpy change which occurs when the certain number of moles of reactants as indicated by the balanced chemical equation, react together completely to give the products under standard condition. $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(\ell)}$ $\Delta H^\circ = -285.8 kJmol^{-1}$	ΔH°
Enthalpy of formation	The change of enthalpy when one mole of the compound is formed from atoms of its elements. $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H^\circ_f = -393.7 kJmol^{-1}$	ΔH°_f
Enthalpy of atomization	The enthalpy change when one mole of gaseous atoms are formed from a molecule or an element under standard conditions. $1/2H_{2(g)} \rightarrow H_{(g)}$ $\Delta H^\circ_{at} = -218 kJmol^{-1}$	ΔH°_{at}
Enthalpy of neutralization	The amount of heat evolved when one mole of hydrogen ions H^+ from an acid, react with one mole of hydroxide ions (OH^-) from a base to form one mole of water. Example:- The enthalpy of neutralization of sodium hydroxide by hydrochloric acid is $-57.4 kJmol^{-1}$ $NaOH + HCl \rightarrow NaCl + H_2O$ $\Delta H_n = -57.4 kjmol^{-1}$	ΔH°_n
Enthalpy of combustion	The enthalpy change when one mole of a substance is completely burnt in excess of oxygen under standard conditions. $C_2H_5OH_{(\ell)} + 3O_2 \rightarrow 2CO_{2(g)} + 3H_2O_{(\ell)}$ $\Delta H^\circ_c = -1368 kJmol^{-1}$	ΔH°_c
Enthalpy of solution	The amount of heat absorbed or evolved when one mole of a substance is dissolved in so much solvent that further dilution results in no detectable heat change. $NH_4Cl_{(s)} + (aq) \rightleftharpoons NH_4Cl_{(aq)}$ $\Delta H^0_{(sol)} = +16.2 kJmol^{-1}$	$\Delta H^\circ_{sol.}$

Enthalpy (energy) changes
Δ (delta means difference)
H (means enthalpy)
$\Delta H = E_{IN} - E_{OUT}$ (joules)

Examples of reactions when ΔH° = +ive :	Examples of reactions when ΔH° = - ive :	Examples of reactions when ΔH° = + ive or -ive :
i) Enthalpy of atomization (ΔH°_{at})	i) Enthalpy of Neutralization (ΔH°_n)	i) Enthalpy of Formation (ΔH°_f)
ii) Enthalpy of ionization (ΔH°_i)	ii) Enthalpy of Combustion (ΔH°_c)	ii) Enthalpy of Solution (ΔH°_{sol})

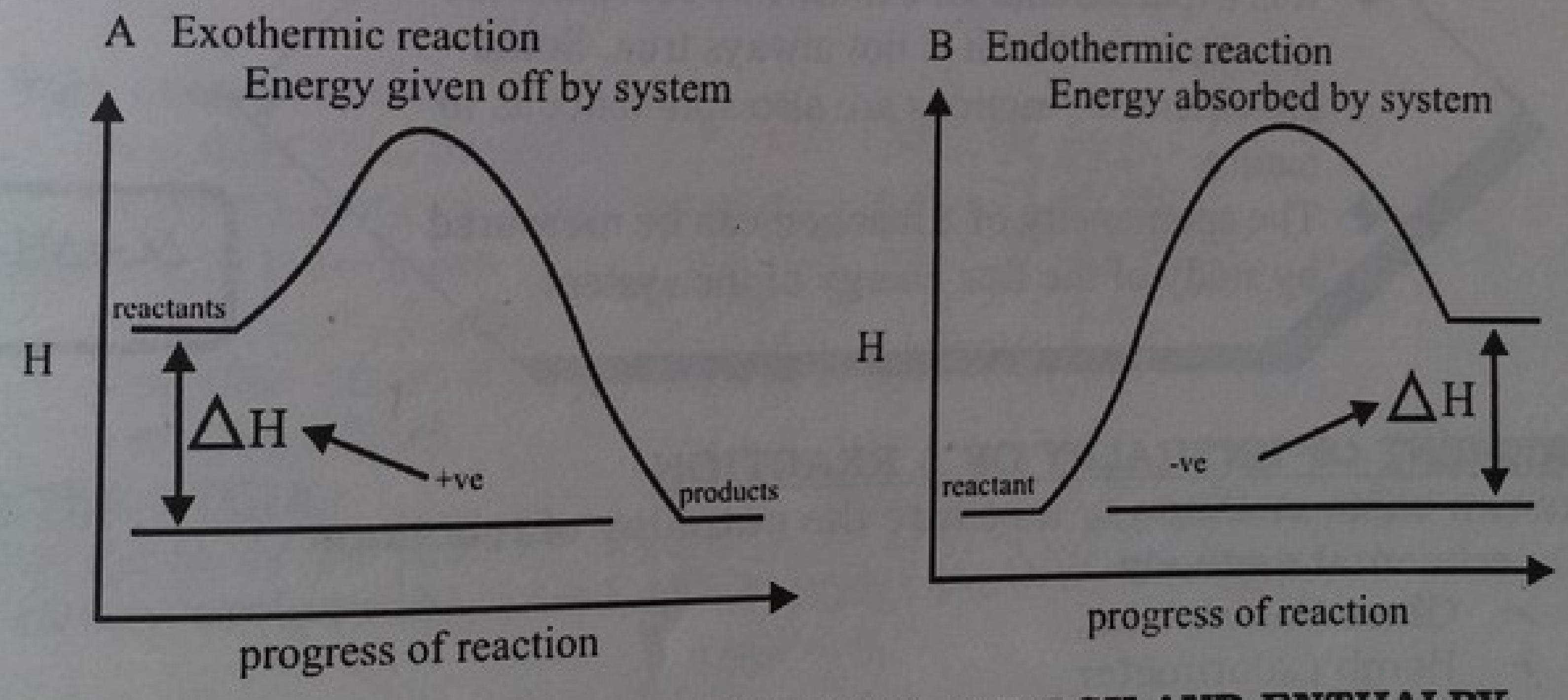
Chapter 7

Thermochemistry

Comparison of Exothermic & Endothermic Reactions

Sr.	Properties	Exothermic	Endothermic
1	Flow of heat energy	System to surrounding	Surrounding to system
2	Temperature of surrounding	Increases	Decreases
3	Temperature of the system	Decreases	Increases
4	Energy of products	Low	High
5	Energy of reactants	High	Low
6	Strength of bonds in products	Strong	Weak
7	Strength of bonds in reactants	Weak	Strong
8	Enthalpy change (ΔH)	Negative	Positive
9	Examples	$C + O_2 \rightarrow CO_2$ $\Delta H = -393.7 kj/mol$ **Respiration** $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ **Neutralization** $NaOH + HCl \rightarrow NaCl + H_2O$	$N_2 + O_2 \rightarrow 2NO$ $\Delta H = +180.51 kj/mol$ **Thermal decomposition** $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ **Dissolving** $NH_4NO_3(s) \rightarrow NH_4NO_3(aq)$

Graphical Representation of Exothermic & Endothermic Reactions



DIFFERENCE BETWEEN INTERNAL ENERGY AND ENTHALPY

Internal energy	Enthalpy
• It is defined as the total energy of the system. • It is denoted by 'E' • It is the sum of kinetic and potential energies. • It is calculated by the formula. $E = \frac{1}{2}mv^2 + P.E$ • It is expressed in Joules or calories.	• It is defined as the sum of internal energy and product of pressure and volume of the system. • It is denoted by 'H'. • It is calculated by the formula. $H = E + PV$ • It is expressed in kcal mol^{-1} or $kJmol^{-1}$.

DIFFERENCE BETWEEN SPONTANEOUS AND NON-SPONTANEOUS REACTIONS

Spontaneous reaction	Non-Spontaneous reaction
• A process which takes place on its own without any outside assistance is called spontaneous reaction. • It moves from a non equilibrium state towards an equilibrium state. • It is usually exothermic in nature. • It is unidirectional irreversible and a real process. **Examples** i. Water flows from higher level to the lower level. ii. Neutralization of a strong acid with a strong base is a spontaneous acid base reaction.	• A process which needs external assistance to start is called non-spontaneous reactions. • It is the reverse of spontaneous process. • It is usually endothermic in nature. • It is multidirectional, reversible and an imaginary process. **Examples** i. Pumping of water uphill. ii. Transfer of heat from cold interior part of the refrigerator to the hot surroundings

ΔG = +ve → non-spontaneous reaction

ΔG = -ve → spontaneous reaction

Do Not Mix

- It is expected that all exothermic reactions are spontaneous. But it is not always true. Some endothermic reactions are also spontaneous in nature.
- The spontaneity of a reaction can be measured by study of the free energy of the system.

$\Delta G = \Delta H - \Delta TS$

MEASUREMENT OF ENTHALPY OF A REACTION

There are two basic methods to measure the enthalpy of reactions

- Experimental methods
  - Glass Calorimeter
  - Bomb Calorimeter
- Theoretical methods
  - Hess's Law for constant heat summation
  - Born Haber's cycle

Heat of reaction of those reactions can be measured by calorimeter, which are in single step.

BY GLASS CALORIMETER

- Glass calorimeter is used to measure the enthalpy of reaction.
- By using following relationship, heat of reaction is calculated.

$$q = m \times s \times \Delta T$$

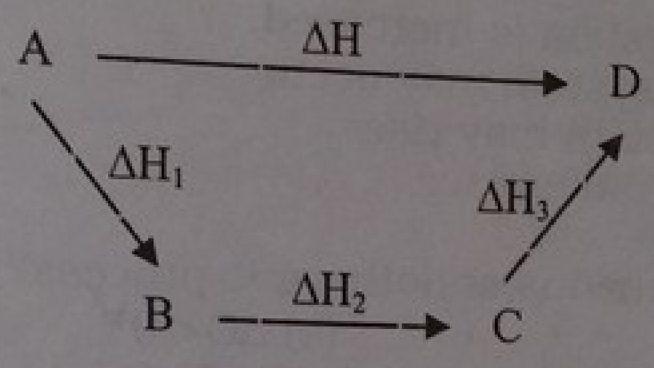
where m=mass of reactant
s =specific heat of reacting mixture
ΔT =change in temperature.

BY BOMB CALORIMETER

- It gives more accurate enthalpy of combustion for food, fuel etc.
- It contains steel vessel lined with enamel to prevent corrosion.
- Platinum crucible is used inside bomb calorimeter.
- Pressure of O_2 is maintained at 20 atm.
- When mass of reactants is in grams, then specific heat unit will be kJ/g.

HESS'S LAW OF CONSTANT HEAT SUMMATION

Energy contents of a reaction remain constant either that reaction completes in single step or different steps.



$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Example

⇒ **Single step process**

$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$ $\Delta H_1 = -89.08$ KJ

⇒ **Two step process**

$NaOH + CO_2 \rightarrow NaHCO_3$ $\Delta H_2 = -48.06$ KJ
$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O$ $\Delta H_3 = -41.02$ KJ

According to Hess's law

$\Delta H_1 = \Delta H_2 + \Delta H_3$
$-89.08 = -48.06 - 41.02$
$-89.08 = -89.08$

BORN-HYBER CYCLE

Energy change in cyclic process is always zero. It enables us to calculate the lattice energy of binary compounds (ionic); this is called Born-Hyber cycle.

$$\sum(\Delta H)\,\text{cycle} = 0$$

LATTICE ENERGY

- Lattice energy of an ionic crystal is the enthalpy of formation of one mole of the ionic compound from gaseous ions under STP.
- Lattice energy cannot be determined directly.
- Lattice energy can be obtained by means of Born-Haber cycle.
- Lattice energy is helpful in discussing structure, bonding and properties of ionic compounds.

Applications

It is applied to determine

- Structure of ionic compounds
- Bonding in ionic compounds
- Properties of ionic compounds

PRACTICE EXERCISE

20 mins
Time Yourself

1. Which one is not a state function
   (a) Internal energy (b) Enthalpy
   (c) Gibbs free energy (d) Work ✓
2. If ΔH value is less than zero than reaction will be
   (a) Exothermic
   (b) Endothermic
   (c) May or may not be Exothormic or Endothermic
   (d) None of these
3. If internal energy of the system is increased.
   (a) Change in state of the system may occur
   (b) Temperature of the system may rise
   (c) Chemical reaction may take place
   (d) All.
4. Which is true for a spontaneous endothermic process?
   (a) $\Delta H<0$ (b) $\Delta G< 0$ ✓
   (b) $\Delta S<0$ (d) $\Delta G>0$
5. A reaction has values of ΔH and ΔS which are both positive. The reaction
   (a) Is spontaneous. (b) Spontaneity is temperature dependent.
   (c) Has an increasing free energy (d) Is non-spontaneous ✓
6. _______ is study about energy of a chemical system
   (a) thermochemistry (b) thermodynamics
   (c) chemical kinetics (d) stoichiometry
7. The environment in which a system is studied is
   (a) state function (b) phase
   (c) surrounding (d) state
8. Unit of heat in SI system is
   (a) J (b) KCal
   (c) Cal (d) GJ
9. Anything which depends upon initial and final state of a system is
   (a) environment (b) surrounding
   (c) state function (d) enthalpy
10. Total energy of a system is
    (a) P.E +K.E. (b) P.E+heat energy
    (c) K.E+heat energy (d) P.E +mechanical energy
11. Mathematical form of first law of thermodynamics is
    (a) $\Delta H=q_p$ (b) $\Delta E=q + w$ ✓
    (c) $\Delta E=q \times v$ (d) of the above
12. Reaction in which heat evolves is called
    (a) endothermic (b) spontaneous
    (c) non-spontaneous (d) exothermic
13. $CuSO_4+Zn \rightarrow ZnSO_4+Cu$ is
    (a) Spontaneous reaction (b) Non-spontaneous reaction
    (c) Endothermic (d) Exothermic
14. Pumping of water uphill is
    (a) spontaneous process (b) non-spontaneous process
    (c) irreversible process (d) reversible process

15. State function, the macroscopic property of system, depends upon
(a) path of reaction
(b) initial state
(c) final state
(d) initial and final state

16. Which one of the following is a state function?
(a) pressure
(b) temperature
(c) enthalpy
(d) all of the above

17. When enthalpy of reactants is higher than product, then reaction will be
(a) endothermic
(b) spontaneous
(c) non-spontaneous
(d) exothermic

18. Enthalpy of a reaction can be measured by
(a) glass calorimeter
(b) manometer
(c) Barometer
(d) thermometer

19. Enthalpy of combustion for food, fuel and other compounds can be measured accurately by
(a) glass calorimeter
(b) bomb calorimeter
(c) thermometer
(d) manometer

20. The lattice energy of NaCl is
(a) –787KJ/mole
(b) 787J/mole
(c) 780KJ/mole
(d) 790KJ/mole

21. Most of thermodynamic parameters are
(a) system
(b) surrounding
(c) phase
(d) state functions

22. ΔH of a system can be calculated by which of following relationship
(a) $q=m \times s \times \Delta T$
(b) $q=\Delta E$
(c) $q=m \times v \times \Delta T$
(d) $q=pv$

23. Change in enthalpy(H) of a system can be calculated by following relationship.
(a) $\Delta H=\Delta E+P\Delta V$
(b) $\Delta H=\Delta E-PV$
(c) $\Delta H=\Delta E-q$
(d) $\Delta H=\Delta E+q$

24. Which of the following is correct
(a) $q_p>q_v$
(b) $\Delta E<\Delta H$
(c) $\Delta E>\Delta H$
(d) Both a & b

25. Two fundamental ways to transfer energy are
(a) pressure and temperature
(b) pressure and volume
(c) heat and work
(d) heat and volume

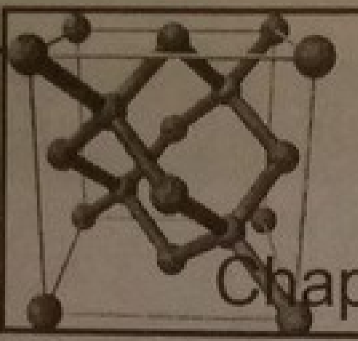
26. which of the following processes has always ΔH = -ve
(a) formation of compound
(b) combustion
(c) dissolution of ionic compound
(d) dilution of a solution

27. Enthalpy change can be
(a) calculated by Hess's law
(b) can be measured by calorimeter
(c) both a and b
(d) none

28. If there is interconversion of solid and liquid states then
(a) $\Delta V = 0$ negligible not zero
(b) $\Delta H \approx \Delta E$
(c) $\Delta H > \Delta E$
(d) both a & b

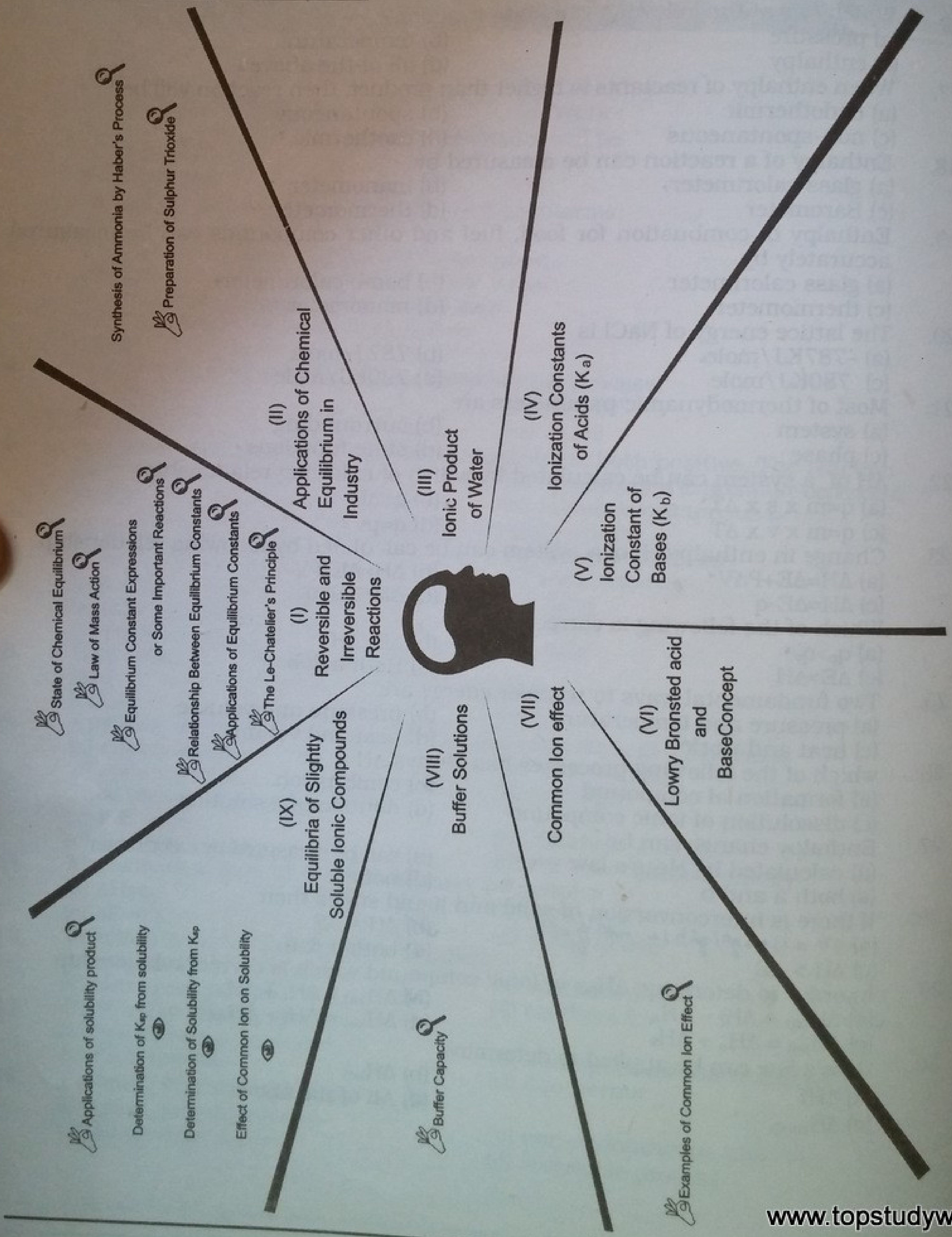
29. In order to determine ΔH_{latt} of ionic compound which is correct relationship
(a) $\Delta H_{latt} = \Delta H_f - \Delta H_x$
(b) $\Delta H_{latt} = \Delta H_f + \Delta H_x$
(c) $\Delta H_{latt} = \Delta H_a + \Delta H_v$
(d) $\Delta H_{latt} = \Delta H_f - \Delta H_{sol}$

30. Hess's law can be applied to determine
(a) ΔHf
(b) ΔH_{latt}
(c) ΔH_{comb}
(d) All of the above



Chapter 8

CHEMICAL EQUILIBRIUM



(I) Reversible and Irreversible Reactions
- State of Chemical Equilibrium
- Law of Mass Action
- Equilibrium Constant Expressions or Some Important Reactions
- Relationship Between Equilibrium Constants
- Applications of Equilibrium Constants
- The Le-Chatelier's Principle

(II) Applications of Chemical Equilibrium in Industry
- Synthesis of Ammonia by Haber's Process
- Preparation of Sulphur Trioxide

(III) Ionic Product of Water

(IV) Ionization Constants of Acids (K_a)

(V) Ionization Constant of Bases (K_b)

(VI) Lowry Bronsted acid and BaseConcept

(VII) Common Ion effect
- Examples of Common Ion Effect

(VIII) Buffer Solutions
- Buffer Capacity

(IX) Equilibria of Slightly Soluble Ionic Compounds
- Applications of solubility product
- Determination of K_{sp} from solubility
- Determination of Solubility from K_{sp}
- Effect of Common Ion on Solubility

RATE OF CHEMICAL REACTION

The change in the molar concentration of the reactants or products per unit time is called rate of chemical reaction.

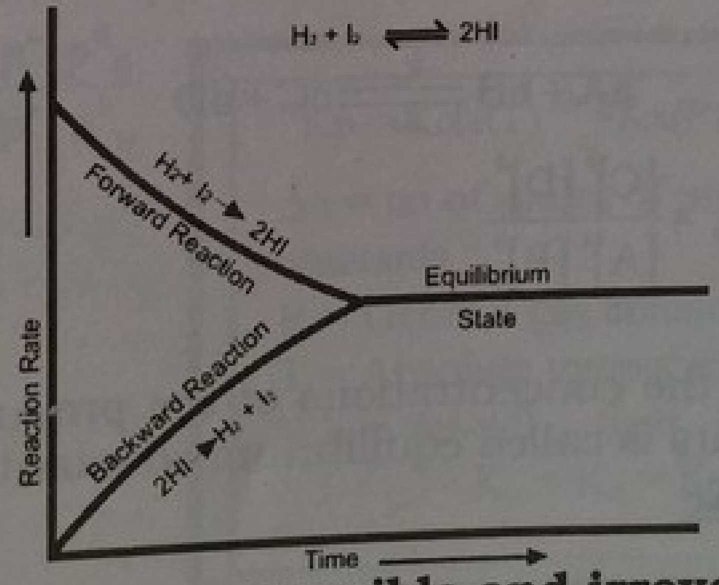
Its units are mol.dm^{-3}s^{-1}.

CHEMICAL EQUILIBRIUM

An apparent state of rest in a reversible chemical reaction where the rate of forward chemical reaction becomes equal to the rate of reverse reaction is called chemical equilibrium.

- **Characteristics of Chemical Equilibrium:**
  - It is established only in close system
  - It can be established from either side
  - It is a microscopic property
  - When chemical equilibrium is established even then minute changes continuously take place. These changes are called microscopic properties.
  - It is a dynamic state.
- **Types of Equilibria**

Homogeneous Equilibrium	Heterogeneous equilibrium
A chemical equilibrium in which the reaction mixture and catalyst are in the same phase is called a homogeneous equilibrium e.g. $2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{NO_{(g)}} 2SO_{3(g)}$	A chemical equilibrium in which the reaction mixture and catalyst are present in different phases is called a heterogeneous equilibrium e.g. $2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{V_2O_{5(s)}} 2SO_{3(g)}$



Difference between reversible and irreversible reaction

Reversible Reactions	Irreversible Reactions
Proceed in both directions i.e. forward and reverse	Proceed in one direction i.e. forward.
Reaction does not go to completion.	Reaction goes to completion usually.
represented by ($\rightleftharpoons$)	represented by ($\rightarrow$)
Dynamic equilibrium state is present	Dynamic equilibrium state is absent.
Examples $N_2 + 3H_2 \xrightleftharpoons{Fe/450^\circ C} 2NH_3$ $PCl_5 \xrightleftharpoons{\text{High Presssure}} PCl_3 + Cl_2$	**Examples** $2Na + 2H_2O \rightarrow 2NaOH + H_2$ $2H_2 + O_2 \rightarrow 2H_2O$

LAW OF MASS ACTION

C.M Guldberg and P.Waage introduced this law in 1864.

Statement:

It states that the rate at which the reaction proceeds is directly proportional to the product of the active masses of the reactants or their molar concentration.

Explanation:

Consider a general reaction in which A and B are the reactants and C and D are the products.

$$A + B \underset{K_r}{\overset{K_f}{\rightleftharpoons}} C + D$$

$$R_f \propto [A][B]$$

$$R_f = K_f\,[A][B]$$

$$R_r \propto [C][D]$$

$$R_r = K_r\,[C][D]$$

$$R_f = R_r$$

$$k_f[A]\,[B] = k_r\,[C]\,(D]$$

Active mass means the concentration in mole dm^{-3} of the reactants which alter as a result of chemical reaction

On rearranging, we get

$$\frac{k_f}{k_r} = \frac{[C][D]}{[A][B]}$$

$$\frac{k_f}{k_r} = K_c$$

$$K_c = \frac{[C][D]}{[A][B]}$$

The constant K_c is called the equilibrium constant of the reaction.

For a more general reaction

$$aA + bB \underset{K_r}{\overset{K_f}{\rightleftharpoons}} cC + dD$$

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

WHAT IS K_c

The ratio of the products of the concentrations of the products to the product of the concentrations of the reactants is called equilibrium constant (K_c)

CHARACTERISTICS OF K_C

Factors	Expression
Depends upon	Greater the temperature, greater will be the K_c value for endothermic reactions and vice versa
Independent of	• Initial concentration of reactants • Direction of reaction • Catalyst
Units	• When Number of moles of reactants = number of moles of products Then Kc has no units • When Number of moles of reactants ≠ number of moles of products Then K_c has some units either conc. Or $(conc)^{-1}$

EQUILIBRIUM CONSTANT EXPRESSIONS OF DIFFERENT REACTIONS

Particular	Ester formation	Dissociation of PCl_5	Decomposition of N_2O_4	Synthesis of NH_3
Reaction	$RCOOH+ROH \rightarrow RCOOR+H_2O$	$PCl_5 \rightarrow PCl_3+Cl_2$	$N_2O_4 \rightarrow 2NO_2$	$N_2+3H_2 \rightarrow 2NH_3$
Initial conc. of reactants	(a) RCOOH (b) ROH	(a) PCl_5	(a) N_2O_4	(a) N_2 (b) H_2
Final conc. of reactants	(a-x) RCOOH (b-x) ROH	(a-x) PCl_5	(a-x) N_2O_4	(a-x) N_2 (b-3x) H_2
Rate expression	$K_c=\frac{[RCOOR][H_2O]}{[RCOOH][ROH]}$ $K_c=\frac{x^2}{(a-x)(b-x)}$	$K_c=\frac{[PCl_3][Cl_2]}{[PCl_5]}$ $K_c=\frac{x^2}{V(a-x)}$	$K_c=\frac{[NO_2]^2}{[N_2O_4]}$ $K_c=\frac{4x^2}{V(a-x)}$	$K_c=\frac{[NH_3]^2}{[N_2][H_2]^3}$ $K_c=\frac{4x^2V^2}{(a-x)(b-3x)^3}$

RELATION BETWEEN DIFFERENT EQUILIBRIUM CONSTANTS

When concentrations are expressed in mole dm^{-3}, then

$$aA + bB \rightleftharpoons cC + dD$$

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$K_c = \frac{C^c{}_C C^d{}_D}{C^a{}_A C^b{}_B}$$

In case of gases, we use partial pressure and K_c changes to K_p.

$$K_c = \frac{p^c{}_C p^d{}_D}{p^a{}_A p^b{}_B}$$

$Kp = Kc(RT)^{\Delta n} = Kx(P)^{\Delta n} = Kn(P/N)^{\Delta n}$

Δn = no of moles of products-no of moles of reactants

R = General gas constant

T = Absolute temperature

When $\Delta n = 0$ then

$$K_p = K_c = K_x = K_n$$

Applications of K_c:

Direction of Reaction	Extent of reaction
• When $K_c<1$, then backward reaction will be dominant before the equilibrium is reached • When $K_c>1$, then forward reaction will dominant before the equilibrium is reached • When $K_c = 1$, then reaction is at equilibrium	• Larger value of K_c favours forward reaction. $2O_3 \rightleftharpoons 3O_2$ ($Kc=10^{55}$ at 25°C) • Smaller value of K_c favours backward reaction $2HF \rightleftharpoons H_2 + F_2$ ($Kc = 10^{-13}$ at 2000°C) • Neither very small nor very large value of Kc favour equilibrium. $N_2 + 3H_2 \rightleftharpoons 2NH_3$ ($Kc= 0.1$ at 25°C)

Characteristics of K_c:

- K_c is independent of the initial concentrations
- K_c changes with change in temperature
- K_c may or may not have units
  - a) Kc has no unit when $\Delta n = 0$
  - b) K_c has certain unit when $\Delta n \neq 0$

    (Δn = no of moles of products – no of mole of reactants)

Note

If K_c is very small then products will be very much unstable.
If K_c is very large then the products will be very much stable.

THE LE-CHATELIER'S PRINCIPLE

Statement

This principle states that if a stress is applied to a system at equilibrium, the system acts in such a way so as to nullify, as far as possible, the effect of that stress.

Applications of Le-Chatelier's principle

There are four aspects

(i) Effect of change of concentration.
(ii) Effect of change of pressure.
(iii) Effect of change of temperature.
(iv) Effect of catalyst on equilibrium.

Effect of change of concentration

- The addition of substance among the reactants, or the removal of a substance among the products at equilibrium stage disturbs the equilibrium position and reaction is shifted to forward direction.
- The addition of a substance among the products or the removal of a substance among the reactants will drive the equilibrium towards the backward direction.

Effect of change in pressure or volume

- The change in pressure or volume is important only for the reversible gaseous reactions where the number of moles of reactants and products are not equal.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

$$K_c = \frac{4x^2V}{(a-2x)^2(b-x)}$$

Conclusion

In the above example by increasing pressure, the position of equilibrium will shift towards the forward direction to attain equilibrium and vice versa.

Effect of change in Temperature

i) On Endothermic reactions.

- By increasing the temperature, reaction is favoured in forward direction.
- By decreasing the temperature, reaction is favoured in backward direction.

$$H_2 + I_2 \rightleftharpoons 2HI \quad \Delta H = +ve$$

ii) On Exothermic reactions.

- By decreasing the temperature, reaction is favoured in forward direction.
- By increasing the temperature, reaction is favoured in backward direction.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H = -ve$$

Effect of catalyst on Equilibrium Constant

A catalyst does not affect the equilibrium position and equilibrium constant of the reaction. It increases the rates of both forward and backward reactions, as it reduces the time to attain the equilibrium.

APPLICATIONS OF CHEMICAL EQUILIBRIUM IN INDUSTRY

Particulars	Synthesis of NH_3	Synthesis of SO_3
Introduction	F. Haber prepared in 1933.	In contact process H_2SO_4 is prepared.
Reaction	$N_2+3H_2 \rightleftharpoons 2NH_3 \quad \Delta H = -92.46kJ$	$2SO_2+O_2 \rightleftharpoons 2SO_3 \quad \Delta H = -97.9kJ$
Conditions for maximum production	▪ Removal of ammonia after regular intervals. ▪ Increase in pressure. ▪ Decrease in temperature.	▪ Continuous supply of O_2. ▪ Increase in pressure. ▪ Decrease in temperature.
Catalyst	Pieces of iron crystals are embedded in fused mixture of MgO, Al_2O_3 and SiO_2.	V_2O_5, NO or Pt are used as catalyst.
Favourable conditions	P= 200-300atm T= 673K(400°C)	P= 1atm T= 400-500°C / 650°C.
Others	▪ Equilibrium mixture contain 35% NH_3 by volume. ▪ Ammonia is separated by refrigeration. ▪ 110 million tons ammonia is produced per anum. ▪ 80% is used in fertilizer. ▪ 13% Nitrogen fixation is done by Haber's process.	

IONIC PRODUCT OF WATER

Water undergoes self-ionization as follows and the reaction is reversible.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K_c[H_2O]=[H^+][OH^-]$$

$$K_w = [H^+][OH^-]=10^{-14} \text{ at } 25°C$$

K_w is called ionic product of water or dissociation constant of water.

K_w VARIES WITH TEMPERATURE

Temperature (°C)	K_w
0	0.11×10^{-14}
10	0.30×10^{-14}
25	1.0×10^{-14}
40	3.00×10^{-14}
100	7.5×10^{-14}

pH

The negative log of hydrogen ion concentration $[H^+]$ is called pH

$$\mathbf{pH = -log[H^+]}$$

- The idea of pH and pOH was introduced by a Danish biochemist, **Sorenson**, in 1909.
  - pH means potential of hydrogen ion concentration
  - pOH means potential of hydroxyl ion concentration

pOH

The negative log of hydroxyl ion concentration $[OH^-]$ is called pOH.

$$\mathbf{pOH = -log[OH^-]}$$

Conclusion:

For neutral water

$$pH = -\log 10^{-7} = 7$$
$$pOH = -\log 10^{-7} = 7$$

pH = 7, → solution is neutral
pH < 7, → solution is acidic
pH > 7, → solution is basic

pK_w

The negative log of K_w is called pK_w

$$\mathbf{pK_w = -log\ K_w}$$

APPROXIMATE pH OF SOME COMMON MATERIALS AT 25°C

Material	pH	Material	pH
1.0MHCl	0.1	Bread	5.5
0.1M HCl	1.1	Potatoes	5.8
0.1M CH_3COOH	2.9	Rainwater	6.2
Gastric juice	2.0	Milk	6.5
Lemons	2.3	Saliva	6.5-6.9
Vinegar	2.8	Pure water	7.0
0.1M $NaHCO_3$	8.4	Eggs	7.8
Soft drinks	3.0	Apples	3.1
Cherries	3.6	Seawater	8.5
Tomatoes	4.2	Milk of magnesia	10.5
Bananas	4.6	0.1M NH_3	11.1
Grapefruit	3.1	0.05M Na_2CO_3	11.6
Oranges	3.5	0.1M NaOH	13.0

IONIZATION CONSTANT OF ACIDS (K_a)

The dissociation constant of an acid is the ratio of the product of molar concentration of the ionized species to the molar concentration of unionized species.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

- Dissociation constant of an acid shows the strength of an acid.
- When $K_a < 10^{-3}$, acid is weak.
- When $K_a = 1$to 10^{-3}, acid is moderately strong.
- When $K_a > 1$, acid is strong.
- Percentage of ionization= $\frac{\text{Amount of an acid ionized}}{\text{Acid initially available}} \times 100$

DISSOCIATION CONSTANTS OF SOME ACIDS AT 25°C

Acid	K_a	Relative strength
HCl	Very large	Very strong
HNO_3	Very large	Very strong
H_2SO_4	Large	Very strong
HSO_4^-	1.3×10^{-4}	Strong
HF	6.7×10^{-5}	Weak
CH_3COOH	1.85×10^{-5}	Weak
$H_2CO_3(H_2O+CO_2)$	4.4×10^{-7}	Weak
H_2S	1.0×10^{-7}	Weak
NH_4^+	5.7×10^{-10}	Weak
HCO_3^-	4.7×10^{-11}	Weak
H_2O	1.8×10^{-16}	Very weak

IONIZATION CONSTANT OF BASES (K_b)

The dissociation constant of a base is the ratio of the product of molar concentration of the ionized species to the molar concentration of unionized species.

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

$$K_b = \frac{[HA][OH]}{[A^-]}$$

- Strength of base is expressed by K_b.
- Any substance that accepts H^+ or generates OH^- is a base.

DISSOCIATION CONSTANTS OF SOME BASES AT 25°C

Base	K_b	Relative strength
NaOH	Very high	Very strong
KOH	Very high	Very strong
$Ca(OH)_2$	High	Strong
NH_4OH	1.81×10^{-5}	Weak
CH_3NH_2(Methylamine)	4.38×10^{-4}	Weak
$C_6H_5NH_2$ (Aniline)	4.7×10^{-10}	Very weak

pK_a and pK_b

The value of pK_a and pK_b can be defined and related as follow:-

$$pK_a = -\log K_a$$
$$pk_b = -\log K_b$$

Conclusion

- Larger the pK_a weaker is the acid and vice versa.
- Larger the pK_b weaker is the base and vice versa.
- If the difference of pK_a value of the two acids is one, then acid with smaller pK_a is ten times stronger than the other.

LOWRY BRONSTED ACID AND BASE CONCEPT

Acid Those species which donate the proton or have a tendency to donate protons are called acids.	**Points to be Remembered:** ➢ Smaller is pKa value stronger is the acid. ➢ Smaller the pK_b value stronger is the base. ➢ Conjugate base of a very weak acid is relatively very strong base. ➢ Conjugate acid of a very strong base is relatively very weak acid.
Base Those species which accept the proton or have tendency to accept the proton are called bases.	

Example

$$\underset{\text{(Acid)}}{HA} + \underset{\text{(Base)}}{H_2O} \rightleftharpoons \underset{\substack{\text{Conjugate}\\\text{Acid}}}{H_3O^+} + \underset{\substack{\text{Conjugate}\\\text{Base}}}{A^-}$$

$$K_a \times K_b = [H^+][OH^-]$$

$$K_a \times K_b = K_w = 10^{-14} \text{ at } 25^\circ C$$

$$K_a \propto \frac{1}{K_b}$$

$$pK_a + pK_b = pK_w \ (pK_w = 14, \text{ at } 25^\circ C)$$
$$pK_a + pK_b = 14 \text{ at } 25^\circ C$$

COMMON ION EFFECT

The addition of a common ion to the solution of a less soluble electrolyte suppresses its ionization and the concentration of unionized species increases, which may come out as a precipitates.

Examples

1- The solubility of a less soluble salt $KClO_3$ in water is suppressed by the addition of a more soluble salt KCl by common ion effect.

$$KClO_{3(S)} \rightleftharpoons K^+_{(aq)} + ClO_3^-{}_{(aq)}$$
$$KCl_{(S)} \rightleftharpoons K^+_{(aq)} + Cl^-_{(aq)}$$

2- An addition of NH_4Cl in NH_4OH solution suppresses the concentration of $OH^-_{(aq)}$ due to the presence of a large excess of NH_4^+ from NH_4Cl.

$$NH_4Cl_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + Cl^-_{(aq)}$$
$$NH_4OH_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

BUFFER SOLUTIONS

The solutions, which resist the change in their pH when a small amount of an acid or a base is added to them, are called buffer solutions.

BUFFER CAPACITY

The buffer capacity of a solution is the capability of a buffer to resist the change of pH in a particular range of pH.

Buffer capacity is developed by varying the molarities of its components.

Best Buffer	Ideal Buffer
$pH = pK_a$ $pOH = pK_b$	$pH = 7$ $pOH = 7$

Henderson's Equation for Acidic Buffer

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

Henderson's Equation for Basic Buffer

$$pOH = pK_b + \log\frac{[Salt]}{[Base]}$$

Points to be Remembered

If [salt] = [acid] then pH = pKa

If [salt] > [acid] then pH > pKa

If [salt] < [acid] then pH < pKa

- **Characteristics of Buffer Solutions**
  - i) It has definite pH
  - ii) Its pH does not alter either on keeping for a long time or on dilution.
  - iii) Its pH is very slightly altered by the addition of strong acid or by strong base.
- **Applications**

  The applications of buffer solutions are found in the study of
  - ➢ Clinical analysis
  - ➢ Chemical reactions
  - ➢ Nutrition
  - ➢ Soil sciences
  - ➢ Biochemistry
  - ➢ Molecular biology
  - ➢ Cell biology

SOLUBILITY PRODUCT (Equilibria of Slightly Soluble ionic compounds)

The product of the concentration of ions raised to an exponent equal to the co-efficient of the balanced equation.

General Expression

$$A_xB_y \rightleftharpoons xA^{+y} + yB^{-x}$$

$$K_{sp} = \left[A^{+y}\right]^x\left[B^{-x}\right]^y$$

Examples

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$ $K_{sp} = 1.6\text{x}10^{-5}$

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ $K_{sp} = 1.8\text{x}10^{-10}$

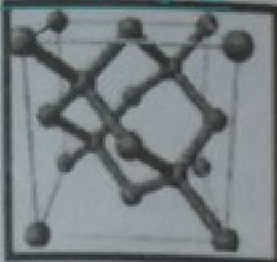
Applications

- Determination of Ksp from solubility of salts
- Determination of solubility from Ksp
- Prediction of precipitation
- Effect of common ion effect on solubility

Applicable for sparingly soluble substances $PbCl_2$, AgCl, $Ca(OH)_2$, $PbCrO_4$.

It is only applicable for those substances whose molar concentrations are less than 0.01.

- **If ionic product = k_{sp}** solution is saturated,
- **If ionic product < k_{sp}** solution is unsaturated,
- **If ionic product > k_{sp}** solution is supersaturated



PRACTICE EXERCISE

30 mins Time Yourself

1. The pH of 10^{-3} mol dm^{-3} of an aqueous solution of H_2SO_4 is
   (a) 3.0
   (b) 2.7
   (c) 2.0
   (d) 1.5
2. Kc value has
   (a) No units
   (b) Units
   (c) Both a & b
   (d) None
3. If a buffer solution of higher pH than seven is to be made we use
   (a) Strong acid and strong base
   (b) Weak acid and strong base
   (c) Weak acid and its salt with strong base
   (d) Weak base and its salt with strong acid
4. Sodium benzoate and benzoic acid are mixed in equimolar ratio to form buffer if pKa is 2 what will be the pH?
   (a) 0
   (b) 1
   (c) 2
   (d) any one
5. AgCl dissolved with conc (2×10^{-2}) Ksp will be
   (a) 3.6×10^{-6}
   (b) 3.6×10^{-5}
   (c) 7.2×10^{-6}
   (d) 4×10^{-4}
6. In which of the following equilibria will Kc and Kp have the same value?
   (a) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
   (b) $N_2 + 3H_2 \rightleftharpoons 2NH_3$
   (c) $2CO + O_2 \rightleftharpoons CO_2$
   (d) $N_2 + O_2 \rightleftharpoons 2NO$
7. Which of the following will not change the concentration of ammonia at the equilibrium?
   (a) Increase of pressure
   (b) Increase of volume
   (c) Addition of catalyst
   (d) Decrease of temperature
8. pH of an aqueous solution is 5.5. The hydroxyl ion conc. in the solution would be
   (a) –5.5
   (b) –8.5
   (c) $10^{-8.5}$
   (d) $10^{8.5}$
9. For a reaction involving only gases at 25°C, the equilibrium constant can be expressed in terms of molarity, Kc, or partial pressure, Kp. Which is true about the numerical value of Kp?
   (a) Kc is generally greaer than Kp
   (b) Kc is generally less than Kp
   (c) Kc is generally equal to Kp
   (d) Kc is equal to Kp if the total moles of reactants and products are equal
10. Which of following is not a base
    (a) KOH
    (b) NH_3
    (c) PH_3
    (d) BF_3
11. Which set of solutes will form a buffer when dissolved in water to make 1 liter of solution?
    (a) 0.0002M HCl
    (b) 0.2 mole of NaCl with 0.2 mole of HNO_3
    (c) 0.4 mole of CH_3COOH with 0.4 mole of NaOH
    (d) 0.4 mole of NH_3 with 0.2 mole of HCl

12. Which one of the following aqueous solutions will be basic?
(a) NaCl
(b) Na_2SO_4
(c) Na_2CO_3
(d) $FeCl_3$

13. The value of Kw in an acidic aqueous solution at 298 K is
(a) $>10^{-14}$
(b) $<10^{-14}$
(c) 10^{14}
(d) 10^{-14}

14. Reaction which proceeds in both directions is called
(a) reversible
(b) irreversible
(c) spontaneous
(d) non-spontaneous

15. Chemical equilibrium state is
(a) dynamic state
(b) static state
(c) free state
(d) unidirectional state

16. Conversion of reactant into product in unit time is called
(a) rate of forward reaction
(b) rate of backward reaction
(c) rate constant
(d) rate co-efficient

17. At start of reaction, the concentration of reactants is
(a) high
(b) low
(c) according to K_c
(d) constant

18. $\frac{[\text{products}]}{[\text{reactant}]} > Kc$ favours
(a) Law of mass action
(b) Rate expression
(c) Forward reaction
(d) Backward reaction

19. Unit of K_c is
(a) $\text{moles}^{2}\text{dm}^{+6}$
(b) $\text{moles}^{-2}\text{dm}^{+6}$
(c) $\text{moles}^{+2}\text{dm}^{-6}$
(d) K_C may or may not have units

20. In case of gases, K_c is replaced by
(a) K_a
(b) K_b
(c) K_p
(d) K

21. Rate expression for ammonia synthesis is
(a) $K_c=x^2/(a-x)(b-x)$
(b) $K_c=x^2/v(a-x)$
(c) $K_c=4x^2/(a-2x)^2(b-x)$
(d) $K_c=4x^2v^2/(a-x)(b-3x)^3$

22. $X_A = \frac{n_A}{n_t}$ is
(a) Mole fraction
(b) Partial pressure
(c) Partial temperature
(d) Molality

23. $\frac{[\text{Product}]}{[\text{Reactant}]} < K_c$
(a) Forward reaction
(b) Backward reaction
(c) Equilibrium stage
(d) Reaction completed

24. When the value of K_c is very small, then
(a) reaction is at start
(b) product conc. is maximum
(c) reactant conc. is minimum
(d) reaction is completed

25. Catalyst used to speed up the reaction of ammonia synthesis is
(a) V_2O_5
(b) V_2O_5 and Pt
(c) Fe
(d) Pieces of Fe crystals are embedded in fused mixture of MgO, Al_2O_3 and SiO_2

26. Temperature for preparation of SO_3 is
(a) 400-500°C
(b) 400°C
(c) 600°C
(d) 200°C

27. By the addition of base in water, pH will be
(a) more than 7 (b) less than 7
(c) equal to 7 (d) no effect

28. Idea of pH and pOH was put forward by
(a) Gibbs (b) Einstein
(c) Sorenson (d) Chadwick

29. Negative log of molar concentration of H^+ ions is called
(a) pH (b) pOH
(c) pKa (d) pKw

30. $Ka<10^{-3}$ means
(a) Very strong base (b) Very weak acid
(c) Very strong acid (d) Very strong salt

31. Any substance which accepts H^+ is base, favours the concept
(a) Lowry's (b) Lewis
(c) Arrhenius (d) None of these

32. Conjugated base of a weak acid is
(a) weak (b) strong
(c) moderately weak (d) unstable

33. When sparingly soluble salt is in equilibrium with molar concentration of its oppositely charged ion then the product is called
(a) common ion effect (b) solubility product
(c) dissociation constant (d) dissociation constant for an acid

34. Solution having the property of a very little change in pH on adding a small amount of strong acid or base is called
(a) buffer solution (b) normal solution
(c) standard solution (d) neutral solution

35. Addition of CH_3COOH and CH_3COONa gives in water
(a) Standard solution (b) buffer solution
(c) acidic buffer solution (d) both b & c

36. Which one of the following is a buffer solution?
(a) brine (b) blood
(c) glue (d) solution of $CuSO_4$

37. Solubility of any salt can be determined from
(a) K_a (b) K_b
(c) K_c (d) K_{sp}

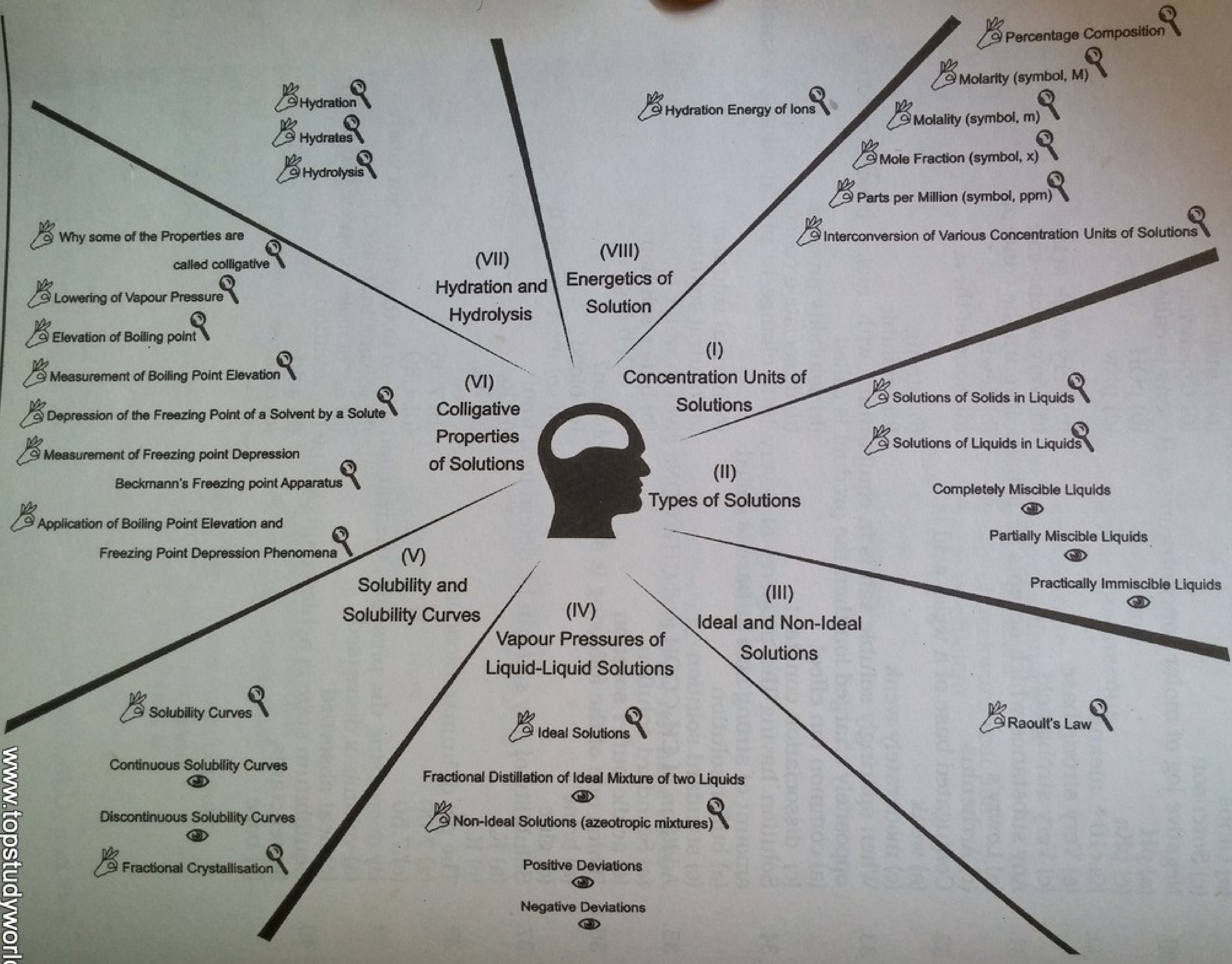
38. The pH of human blood is
(a) 7.00 (b) 7.35
(c) 7.50 (d) 7.80

39. By decreasing the pressure, the reaction will go to that direction where
(a) volume is decreased (b) volume increased
(c) heat absorbed (d) no. of moles of specie decreased

40. Equilibrium state is achieved quickly by the addition of.
(a) reactants (b) acid
(c) base (d) catalyst

Chapter 9

SOLUTIONS


(I) Concentration Units of Solutions
Percentage Composition
Molarity (symbol, M)
Molality (symbol, m)
Mole Fraction (symbol, x)
Parts per Million (symbol, ppm)
Interconversion of Various Concentration Units of Solutions
(II) Types of Solutions
Solutions of Solids in Liquids
Solutions of Liquids in Liquids
Completely Miscible Liquids
Partially Miscible Liquids
Practically Immiscible Liquids
(III) Ideal and Non-Ideal Solutions
Raoult's Law
(IV) Vapour Pressures of Liquid-Liquid Solutions
Ideal Solutions
Fractional Distillation of Ideal Mixture of two Liquids
Non-Ideal Solutions (azeotropic mixtures)
Positive Deviations
Negative Deviations
(V) Solubility and Solubility Curves
Solubility Curves
Continuous Solubility Curves
Discontinuous Solubility Curves
Fractional Crystallisation
(VI) Colligative Properties of Solutions
Why some of the Properties are called colligative
Lowering of Vapour Pressure
Elevation of Boiling point
Measurement of Boiling Point Elevation
Depression of the Freezing Point of a Solvent by a Solute
Measurement of Freezing point Depression
Beckmann's Freezing point Apparatus
Application of Boiling Point Elevation and Freezing Point Depression Phenomena
(VII) Hydration and Hydrolysis
Hydration
Hydrates
Hydrolysis
(VIII) Energetics of Solution
Hydration Energy of Ions

PHASE

Every sample of matter with uniform properties and a fixed composition is called a phase.

SOLUTION

A homogeneous mixture of two or more kinds of different molecular or ionic substances is called solution.

COMPONENTS OF A SOLUTION

Solute

(i) In the case of a solution of a gas or solid dissolved in a liquid, the gas or solid is the solute.
(ii) Generally, the component of a solution, which is in smaller amount, is called solute.

Solvent

(i) In the case of a solution of a gas or solid in a liquid, the liquid is the solvent.
(ii) Generally, the component of a solution, which is in larger amount, is called solvent.

Example

When sodium chloride is dissolved in water, sodium chloride is the solute and water is the solvent.

CONCENTRATION UNITS OF SOLUTIONS

Particular	Percentage composition
Definition	Solute in percent of solvent. Four ways of expression of percentage composition 1- $\frac{W}{W}$% it is a weight of solute dissolved per 100g of solution 2- $\frac{V}{W}$% it is volume of solute (cm^3) dissolved per 100g of solution. 3- $\frac{W}{V}$% it is a weight of solute (g) dissolved per100cm^3 of solution 4- $\frac{V}{V}$% it is volume of solute (cm^3)dissolved per 100 cm^3 of solution
Expression	Expressed by percentage (%).
Units	In volumetric analysis

MOLARITY

The number of moles of a solute dissolved per dm^3 of a solution.

Molar Solution
A solution whose molarity is one e.g. 1M NaOH solution.
(40g/1dm^3 of soln)

Symbol

It is denoted by 'M'.

Examples

0.1M NaOH solution and 0.02M $KMnO_4$ solution

Formulae

1- $$\text{Molarity(M)} = \frac{\text{Moles of solute}}{\text{Volume of solution in dm}^3}$$

2- $$\text{Molarity(M)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Volume of Solution in dm}^3}$$

MOLALITY

Definition

The number of moles of a solute dissolved per kg of a solvent.

Symbol

It is denoted by 'm'.

Example

0.1m NaOH solution, 0.01m HCl etc.

Formulae

1- $$\text{Molality (m)} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}$$

2- $$\text{Molality (m)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Mass of solvent in kg}}$$

Molal Solution

A solution whose molality is one e.g. 1m NaOH solution. (40g/1kg of water)

MOLE FRACTION

Definition

The ratio of the number of moles of a component to the total number of moles of all the components of solution.

Symbol

It is denoted by 'X'.

Explanation

Let us have components A,B and C making a solution and their number of moles are n_A, n_B and n_C respectively. X_A, X_B and X_C are their mole fractions and are given below:-

$$X_A = \frac{n_A}{n_A + n_B + n_C}$$

$$X_B = \frac{n_B}{n_A + n_B + n_C}$$

$$X_C = \frac{n_C}{n_A + n_B + n_C}$$

Normality (N)

The number of gram equivalent of the solute dissolved per dm^3 of a solution.

0.1N NaOH 0.02N $KMnO_4$

- The sum of the mole fractions of all the components of solution must be unity (one).
- To get mole percent mole fractions is multiplied by 100.
- There are no formal units of mole fraction.

PARTS PER MILLION

Definition

The number of parts (by weight or volume) of a solute per million parts (by weight or volume) of the solution.

Symbol

It is denoted by 'ppm'.

$$\text{ppm} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

Chapter 9

Solutions

Formula

Mass Percent	Symbol	Formula
Parts per million	ppm	$\text{ppm} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$
Parts per billion	ppb	$\text{ppb} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^8$
Parts per trillion	ppt	$\text{ppt} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^{11}$

A COMPARISON OF VARIOUS CONCENTRATION UNITS

Name	Symbol	Units	Advantages	Disadvantages
Molarity	M	moles dm^{-3}	Useful in stoichiometry, measure by volume.	Temperature dependent, must know density to find solvent mass.
Molality	m	moles kg^{-1}	Temperature independent, useful in special applications	Measure by mass, must know density to convert to molarity.
Mole Fraction	X	None	Temperature independent, useful in all kinds of solutions.	Measure by mass, must know density to convert to molarity.
Parts Per million	ppm	ppm	Temperature independent, useful for small amount.	Measure by mass, must know density to convert to molarity.

TYPES OF SOLUTION

State of Solute	State of Solvent	Examples
Solid	**Liquid**	**Sugar in water, jellies.**
Solid	Gas	Dust particles in smoke
Solid	Solid	Metal alloys pearls, opals
Liquid	Gas	Mist, fog, clouds
Liquid	Liquid	Alcohol in water, milk
Liquid	Solid	Mercury in silver, butter
Gas	Gas	Air
Gas	Liquid	O_2 in water, CO_2 in water
Gas	Solid	H_2 adsorbed by palladium

Types of solutions on the basis of number of substances

Binary Solution	Ternary Solution	Quaternary Solution
A homogenous mixture of two substances is called binary solution	A homogenous mixture of three substances is called ternary solution	A homogenous mixture of four substances is called quaternary solution
water + sugar	salt + sugar + water	salt + sugar + water + lemon

TOP Study World KIPS

Types on the basis of saturation

Unsaturated Solution	Saturated Solution	Super Saturated Solution
An unsaturated solution is a solution, which contains less amount of solute than is required to saturate it at that temperature.	A solution that can hold no more of the solute at a particular temperature is said to be a saturated solution at that temperature.	Solution that is more concentrated than a saturated solution is known as super saturated solution. If a crystal of solute is added to this solution, the excess of solute crystallizes.

Types on the basis of miscibility

Solution of completely miscible liquids	Solution of partially miscible liquids	Solution of immiscible liquids
Alcohol & Water Alcohol & Ether	Phenol & Water Triethylamine & Water Nicotine & Water	Benzene & Water Carbon disulphide & Water

Upper Consulate Temperature

Water - Aniline system = 167^0C
15% water solution.
Methanol – Cyclohexane = 49.1^0C
29% methanol solution.

Dilute Solution

A solution, which contains relatively lower concentration of solute.

Concentrated Solution

A solution, which contains relatively higher concentration of solute.

PHENOL WATER SYSTEM

- At 25°C, Solution of phenol and water contains two layers.
  - ➢ Upper layer is saturated phenol with water.
    - 5% solution of phenol in water.
      Phenol is solute while water acts as a solvent
  - ➢ Lower layer is saturated water with phenol.
    - 30% solution of water in phenol
      Water is solute while phenol acts as a solvent
- At 65.9°C, the both layers merge in each other to form a homogenous mixture containing 34% phenol & 66% water.
- The temperature at which two conjugated mixtures merge in one another called critical solution temperature or upper consulate temperature.

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IDEAL AND NON-IDEAL SOLUTION

Ideal solution	Non-ideal solution
A – B attractive forces are equal in strength with A – A & B – B attractive forces	A – B attractive forces are not equal in strength with A – A & B – B attractive forces
Volume of solution is equivalent to sum of volumes of all components i.e. $\Delta V = 0$.	Volume of solution is not equal to sum of volumes of all components i.e. $\Delta V \neq 0$
Enthalpy change is zero i.e. $\Delta H = 0$	Enthalpy change is not zero i.e. $\Delta H \neq 0$.
Obeys Raoult's law	Shows deviations from Raoult's law

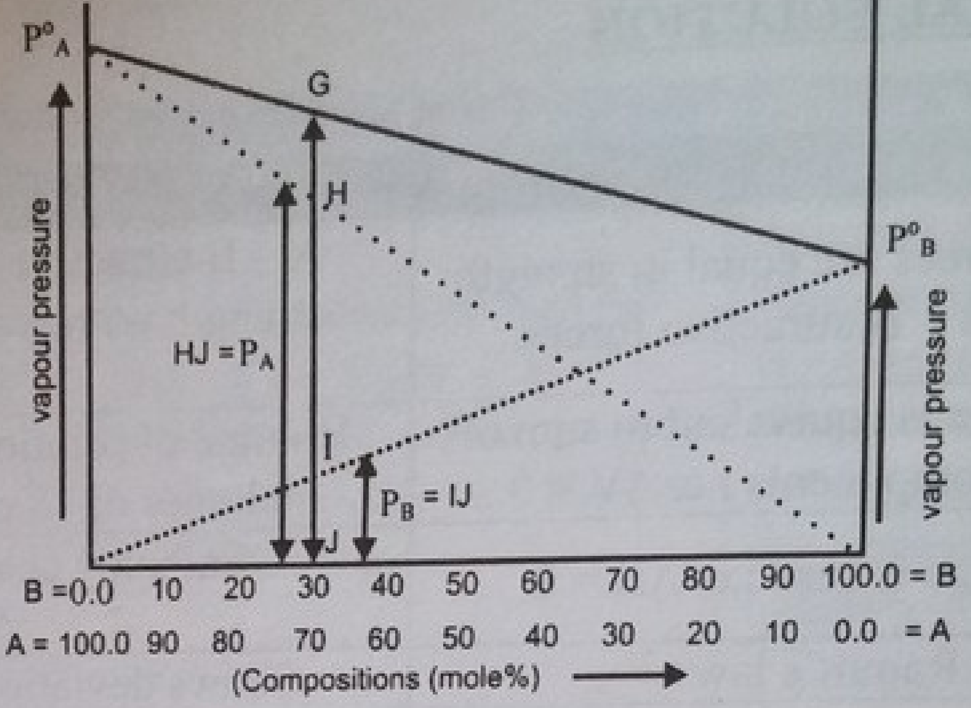
RAOULT'S LAW

Statements	Mathematical Representation	Symbols	Conclusions
The vapour pressure of a solvent above a solution is equal to the product of the vapour pressure of pure solvent and the mole fraction of solvent in solution.	$P = p^\circ x_1$	**p** – vapour pressure of solvent in solution. **p°** – vapour pressure of pure solvent. **x_1** – mole fraction of solvent. **x_2** – mole fraction of solute. **Δp** = lowering of vapour pressure. **$\Delta p / p^\circ$** = relative lowering of vapour pressure	The relative lowering of vapour pressure is:- ➢ Independent of temperature ➢ Dependent on conc. of solute. ➢ constant when equi-molar proportions of different solutes are dissolved in the same mass of same solvent.
The lowering of vapour pressure is directly proportional to the mole fraction of solute.	$\Delta p = p^\circ x_2$		
The relative lowering of vapour pressure is equal to the mole fraction of solute.	$\dfrac{\Delta p}{p^\circ} = X_2$		

Raoult's Law (when both components are volatile)

- Graph is plotted between compositions on x-axis and vapour pressure on y-axis
- If composition of solution is;
  - ➢ Component A is 70% (highly volatile thus low boiling)
  - ➢ Component B is 30% (less volatile thus high boiling)
- P^0_A & P^0_B are partial pressures of pure components.
- If the solution is ideal then straight line will produce in graph.
- At point G P_t of solution will be sum of partial pressures of components i.e.

$$P_t = p_A + p_B$$
$$P_t = (p^0_A - p^0_B)x_A + p^0_B$$



Vapour Pressures of Liquid-Liquid Solutions

Binary mixtures of miscible liquids may be classified as

(i) Ideal solutions
(ii) Non-ideal or real solutions

(i) Ideal Solutions

A solution which obeys Raoult's law is called ideal solution.

Examples

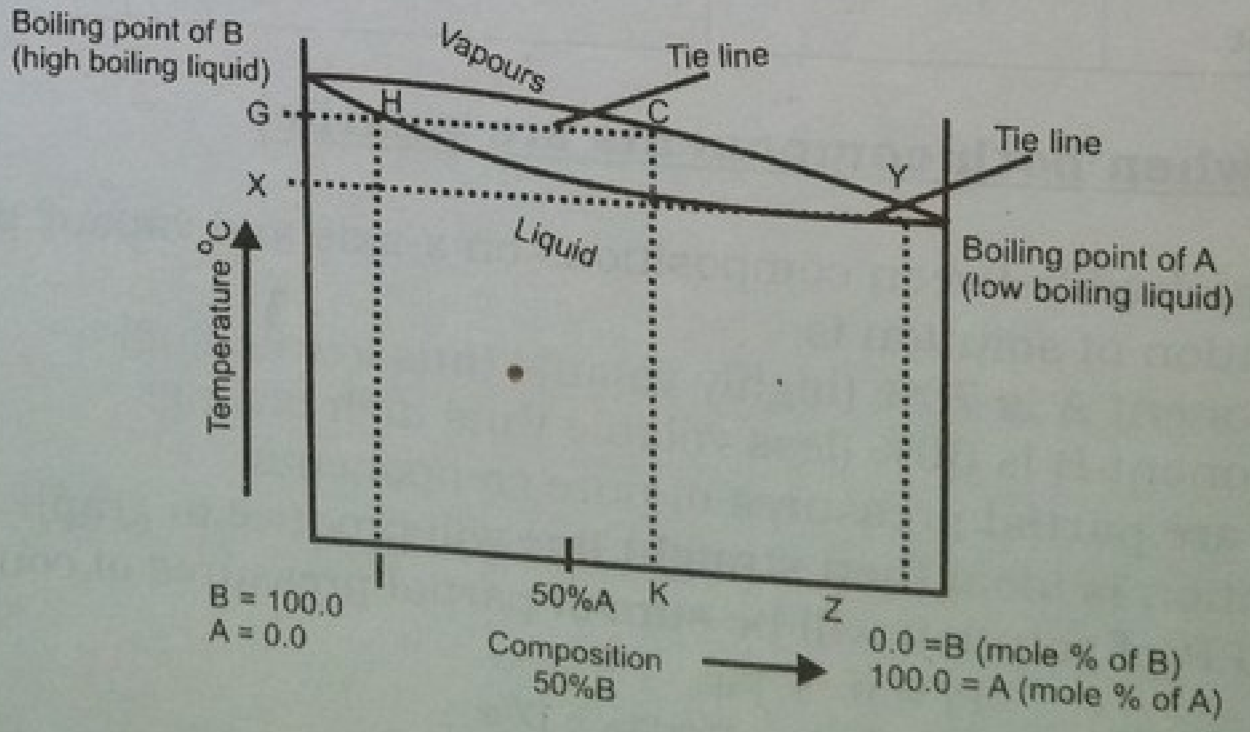
(i) benzene-toluene solution
(ii) benzene ether solution
(iii) chlorobenzene-bromobenzene solution
(iv) ethyl iodide-ethylbromide solution

Zeotropic Mixture

A mixture or solution which distills over with the change in composition is called zeotropic mixture.

Fractional Distillation of Ideal Mixture of two liquids

A technique by which different liquids are separated from each other on the basis of their different boiling points is called fractional distillation.



Non-Ideal Solutions

A solution or mixture which does not obey Raoult's law is called non-ideal solution.

- They show deviations from Raoult's law due to difference in their molecular structures i.e. size, shape and intermolecular forces.
- Formation of such solution is accompanied by changes in volume and enthalpy.

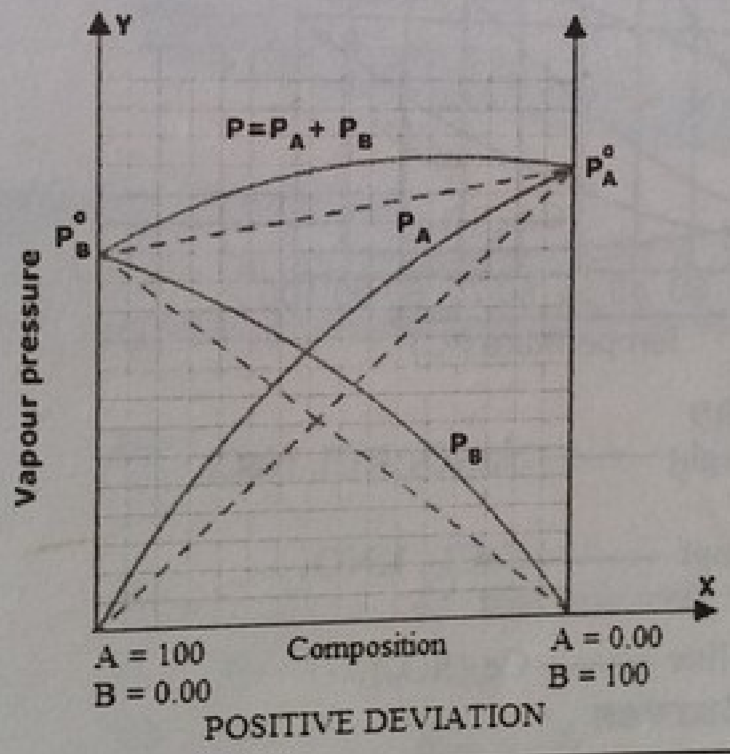
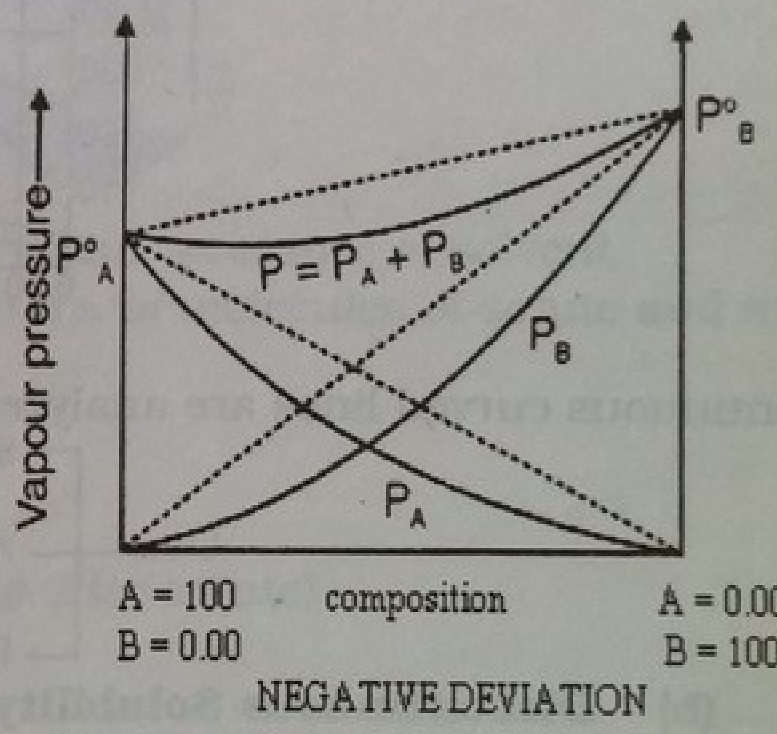
Azeotropic Mixtures

Those mixtures which boil at constant temperature and distil over without change in composition at any temperature like a pure chemical compound are called azeotropic mixtures.

Types of Deviation

The deviation of non-ideal solutions are of two types:-

- Positive deviations
- Negative deviations

	Positive Deviations	Negative Deviations
Definition	When the vapour pressure is greater than that predicted by Raoult's Law	When the vapour pressure is lesser than that predicted by Raoult's Law
Reason	Solute – solvent interaction is weaker than solute – solute or solvent – solvent interaction.	Solute – solvent interaction is stronger than solute – solute or solvent – solvent interaction.
Graphical Representation	 POSITIVE DEVIATION	 NEGATIVE DEVIATION
Examples	Ethanol-water mixture boils at 78.1°C with 4.5% water and 95.5% alcohol. 78.1°C is lower than the boiling point of ethanol (78.5°C) and water (100°C).	Hydrochloric acid solution in water is an example of negative deviation. HCl forms an azeotropic mixture with water, boiling at 110°C and containing 20.24% of the acid.

SOLUBILITY

The concentration of the solute in the solution when it is in equilibrium with the solid substance at a particular temperature is called solubility

OR

Number of grams of solute dissolved in 100g of solvent at a particular temperature is called solubility.

Examples

(i) Saturated solution of NaCl in water at 0°C contains 37.5g of NaCl in 100g of water.

(ii) The solubility of $CuSO_4$ in water at 0°C is 14.3g/100g while at 100°C it is 75.4g/100g.

Factors Affecting Solubility

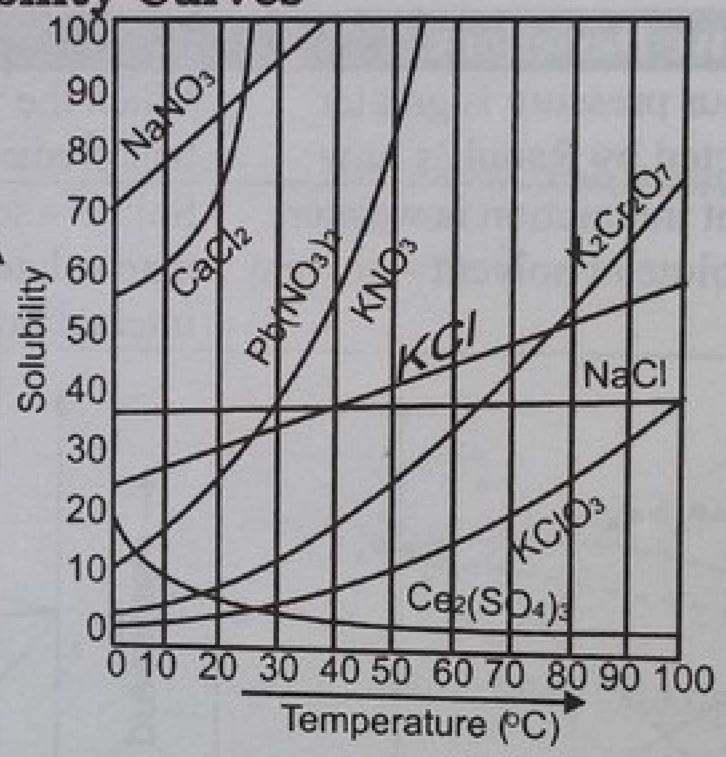
- Nature of solute
- Nature of solvent
- Pressure (in case of gas)
- Temperature

Solubility Curves

A graphical representation between temperature and solubility of its solution is called solubility curves.

Types of Solubility Curves

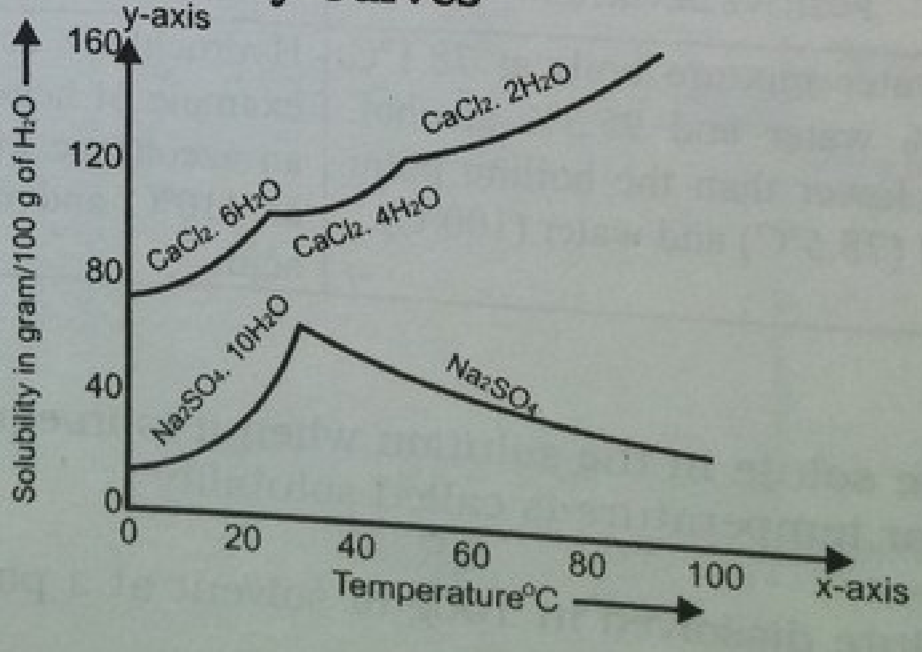
(a) Continuous Solubility Curves



Continuous curved lines are analyzed as

Lines
- Straight — $NaNO_3$, KCl, NaCl
- Abrupt — $CaCl_2$, KNO_3
- Decline — $Ce_2(SO_4)_3$

(b) Discontinuous Solubility Curves



COLLIGATIVE PROPERTIES OF SOLUTIONS

Liquid Properties

Colligative Property

The property which depends upon the number of particles of solute and solvent but independent of the nature of the solute.

Constitutive Property

The property which depends upon the arrangements of atoms in a molecule.

Additive Property

Those properties which are sum of individual component of a substance e.g. molar mass of H_2SO_4

Examples of Colligative Properties

(i) Lowering of vapour pressure
(ii) Elevation of boiling point
(iii) Depression of freezing point
(iv) Osmotic pressure

The word colligative means "bound together in a collection" and is used because a collection of solute particles is responsible for the observed effects.

Conditions for study of colligative properties

(i) Solution should be dilute.
(ii) Solute should be non-volatile.
(iii) Solute should be non-electrolyte.

Lowering of Vapour Pressure

- Addition of solute in solvent decreases the vapour pressure of solvent.
- Lowering of vapour pressure depends upon no. of molecules of solute and mass of solute.

$$\frac{\Delta p}{p^o}=X_2$$

$$\frac{\Delta p}{p^o}=\frac{n_2}{n_1+n_2} \quad \text{(1 for solvent and 2 for solute)}$$

$$\frac{\Delta p}{p^o}=\frac{n_2}{n_1} \quad (n_2 = 0)$$

$$\frac{\Delta p}{p^o}=\frac{n_2}{n_1}=\frac{\dfrac{\text{mass in g of solute}(W_2)}{\text{Molar mass}(M_2)}}{\dfrac{\text{mass in g of solvent}(W_1)}{\text{Molar mass}(M_1)}}$$

$$\frac{\Delta p}{p^o}=\frac{W_2M_1}{M_2W_1}$$

$$M_2=\frac{p^o}{\Delta p}.\frac{W_2M_1}{W_1}$$

Elevation of Boiling point

- Addition of solute in solvent increases the boiling point of solvent.
- Boiling point of H_2O in 0.1 molal solution of urea and glucose will rise by 0.052°C i.e 100.052°C.
- Boiling point elevation value is called molal boiling point constant or ebullioscopic constant denoted by K_b.
- Higher the concentration of solute, greater will be boiling point elevation.

$\Delta T_b = T_2 - T_1$

ΔT_b (Elevation in boiling point)

$\Delta T_b \propto$ molality

$\Delta T_b \propto m$

$\Delta T_b = K_b m$

$$\Delta T_b = K_b . \frac{W_2}{M_2} . \frac{1000}{W_1}$$

$$M_2 = \frac{K_b}{\Delta T_b} \times \frac{W_2}{W_1} \times 1000$$

Measurement of Boiling point elevation

The boiling point elevation can be measured by Landsberger's method. The apparatus consists of four major parts.

(i) An inner tube
(ii) A boiling flask
(iii) An outer tube
(iv) A thermometer (Beckmann's thermometer)

Depression of Freezing point

- Addition of solute in solvent will decrease the freezing point of solvent.
- Freezing point of H_2O will decrease by 1.86°C in solution of urea and glucose i.e −1.86°C.
- Decrease in freezing point is called molal freezing point constant or cryoscopic constant denoted by K_f.

$\Delta T_f = T_1 - T_2$

$\Delta T_f \propto$ molality

$\Delta T_f = K_f m$

ΔT_f is called depression in freezing point

$$\Delta T_f = K_f \frac{1000\, W_2}{M_2 \times W_1}$$

Molar mass of solute (M_2) $= \dfrac{K_f}{\Delta T_f} \dfrac{1000\, W_2}{W_1}$

Measurement of Freezing Point Depression

There are two important methods for the measurement of depression of freezing point.

1. **Beckmann's method.**
2. **Rast's camphor method.**

Beckmann's method.

The apparatus consists of three major parts.

a. A freezing tube.
b. An outer larger tube.
c. A large jar containing a freezing mixture.

No.	Solvent	B.P. (°C)	K_b (°C/m)	F.P. (°C)	K_f (°C/m)
1	Acetic acid	118	3.07	17	3.90
2	Water	100	0.52	0.00	1.86
3	Benzene	80	2.70	5.5	5.10
4	Ethanol	79	1.75	-114.5	1.99
5	Ether	34.4	2.16	-116.3	1.79

ENERGETICS OF SOLUTIONS

The quantity of heat energy, that is absorbed or released when a substance forms solution, is termed as heat of solution.

Enthalpy of Solution

The enthalpy or heat of solution of a substance is defined as the heat change when one mole of the substance is dissolved in a specified number of moles of solvent at a given temperature

HYDRATION

The phenomenon in which water molecules surround and interact with solute ions or molecules is called hydration.

- The number of water molecules surrounding an ion depends upon the charge density of the ion
- Charge density = charge/size, higher the charge density greater will be the number of molecule surrounding it.
  - Positive ion will be surrounded by greater number of water molecules as compare to –ve ion because of its high charge density due to its smaller size.
  - Negative ion will be surrounded by less number of water molecules as compare to +ve ion because it has less charge density due to its larger size.
- The ion which is surrounded by water molecule is called hydrated ion.
- The number of water molecules which surround an ion are called water molecules of hydration.
- The number of water molecules which are part of the crystals are called water of crystallization
- The compounds that have specific number of water molecules are called hydrates.
- Water of crystallization can be removed by heating of substance.

Hydration Energy of Ions

The hydration energy is the amount of heat evolved when one mole a gaseous ions ar dissolved in water to give infinitely dilute solution.

$$H^+(g) + H_2O(l) \rightarrow H^+(aq) \quad \Delta H_h = -1075 \text{ kJ/mol}$$

DROLYSIS

The interactions between salts and water to produce acidic or basic solutions are called hydrolytic reactions and this phenomenon is known as hydrolysis.

The Result of Salt Hydrolysis

No.	Salt made from	Example	Nature of solution
1	Strong acid with high pK_a + Strong base with high pK_b	NaCl, KNO_3, Na_2SO_4	Neutral
2	Strong acid with high pK_a + Weak base with low pK_b	NH_4Cl_3, $AlCl_3$, $CuSO_4$	Acidic
3	Weak acid with low pK_a + Strong base with high pK_b	Na_2CO_3, $NaHCO_3$, CH_3COONa	Alkaline
4	Weak acid with low pK_a + Weak base with low pK_b	CH_3COONH_4	Almost neutral

PRACTICE EXERCISE

25 mins
Time Yourself

1. Which of the following solutions of H_2SO_4 is more concentrated?
(a) 1 molar solution (b) 1 molal solution
(c) 1 normal solution (d) All have same concentration

2. Which of the following unit of concentration is independent of temperature?
(a) Molarity (b) Molality
(c) Mole fraction (d) All

3. Which of the following is an example of liquid in gas solution.
(a) Opals (b) Dust particles in smoke
(c) Paints (d) Fog

4. The molal boiling point constant is the ratio of the elevation of boiling point to
(a) Molarity (b) Molality
(c) Mole fraction of solvent (d) Mole fraction of solute

5. Which of the following are the conditions of colligative properties
(a) Non-electrolyte solute (b) Non-volatile solute
(c) Dilute solution (d) All of the above

6. Which has the minimum freezing point?
(a) One molal NaCl (b) One molal KCl solution
(c) One molal $CaCl_2$ (d) One molal urea solution

7. Which of the following is not a colligative property?
(a) Lowering of vapour pressure (b) Freezing point
(c) Osmotic pressure (d) Elevation of polling point

8. Which of the following substance do not show continuous solubility curve?
(a) $KClO_4$ (b) $Na_2SO_4.10H_2O$
(c) $K_2Cr_2O_7$ (d) $PbCl_2$

9. When common salt is dissolved in water?
(a) Boiling point of water decrease (b) Boiling point of water increase
(c) Boiling point of water remains same (d) None of the above

10. Every sample of matter with uniform properties and fixed composition is called
(a) solute (b) solvent
(c) solution (d) phase

11. Homogeneous mixture of two or more than two compounds is called
(a) solution (b) compound
(c) radical (d) ion

12. The component of solution which is in smaller amount is called
(a) solvent (b) solute
(c) phase (d) ion

13. Solution with maximum concentration of solute at given temperature is called
(a) Super saturated solution (b) unsaturated solution
(c) saturated solution (d) dilute solution

14. 10ml of alcohol dissolve in 90ml of water, unit of concentration used is
(a) % w/w (b) % w/v
(c) % v/v (d) % v/w

15. Number of moles in 1kg of solvent is called
(a) normality
(b) molarity
(c) molality
(d) mole fraction

16. 58.5g of NaCl per $1dm^3$ of solution of NaCl in water, the concentration of solution will be
(a) 0.1M
(b) 1m
(c) 1M
(d) 0.1N

17. In partially miscible liquids, the two layers are
(a) saturated solutions of each liquid
(b) unsaturated solutions of each liquid
(c) normal solution of each liquid
(d) no layer formation takes place

18. If the volume of solution is equal to sum of volumes of its all components then the solution
(a) will be an ideal solution
(b) will be non-ideal solution
(c) will show deviations from Raoult's law
(d) both b & c

19. The relative lowering of vapour pressure is
(a) equal to the mole fraction of solvent
(b) equal to the mole fraction of solute
(c) directly proportional to the mole fraction of solute
(d) both b & c

20. The solution which distils over with change in composition.
(a) ideal solution
(b) zeotropic solution
(c) azeotropic solution
(d) non-ideal solution

21. Mixtures which distill over without change in composition called
(a) zeotropic mixture
(b) azeotropic mixture
(c) amphoteric mixture
(d) ideal solution

22. Concentration of solute molecule when they are in equilibrium with solid substance at particular temperature is called
(a) saturated solution
(b) solubility
(c) unsaturated solution
(d) super saturated solution

23. Solubility of $KClO_3$ gives
(a) continuous and falling solubility curve
(b) discontinuous and falling solubility curve
(c)continuous and rising solubility curve
(d) discontinuous and rising solubility curve

24. The determination of correct molecular weight from Raoult's law is applicable to
(a) a volatile solute in dilute solution
(b) a non-electrolyte & non volatile solute in concentrated solution
(c) a non-electrolyte & non volatile solute in concentrated solute
(d) non volatile solute in a dilute solution

25. Boiling point elevations can be measured by
(a) Beckmann's method
(b) Landsberger's method
(c) Lind's method
(d) none of the above

26. Beckmann's apparatus is used to measure
(a) boiling point elevation
(b) depression in freezing point
(c) lowering of vapour pressure

CH. 17

27. Water molecules surrounds more around
(a) +ve ion (b) complex ion
(c) –ve ion (d) neutral atom

28. The compounds in which water molecules are added are called
(a) Hydrated ions (b) double salts
(c) hydrates (d) complexes

29. Hydration is a process in which
(a) Molecules are surrounded by solvent molecules
(b) Ions are surrounded by solvent molecules
(c) Both ions and molecules are surrounded by solvent molecules
(d) Both ions and molecules are surrounded by water molecules

30. Solution of Na_2SO_4 will be
(a) basic (b) acidic
(c) neutral (d) cannot be predicted without data

31. ppm means
(a) parts of solute in 1000 parts of solvent
(b) parts of solvent in 1000 parts of solute
(c) parts of solute in one million parts of solution
(d) parts of solvent in one million parts of solute

32. 1 molar solution of glucose in water contains weight of glucose
(a) $180 g/dm^3$ (b) $170 g/dm^3$
(c) $190 g/dm^3$ (d) $195 g/dm^3$

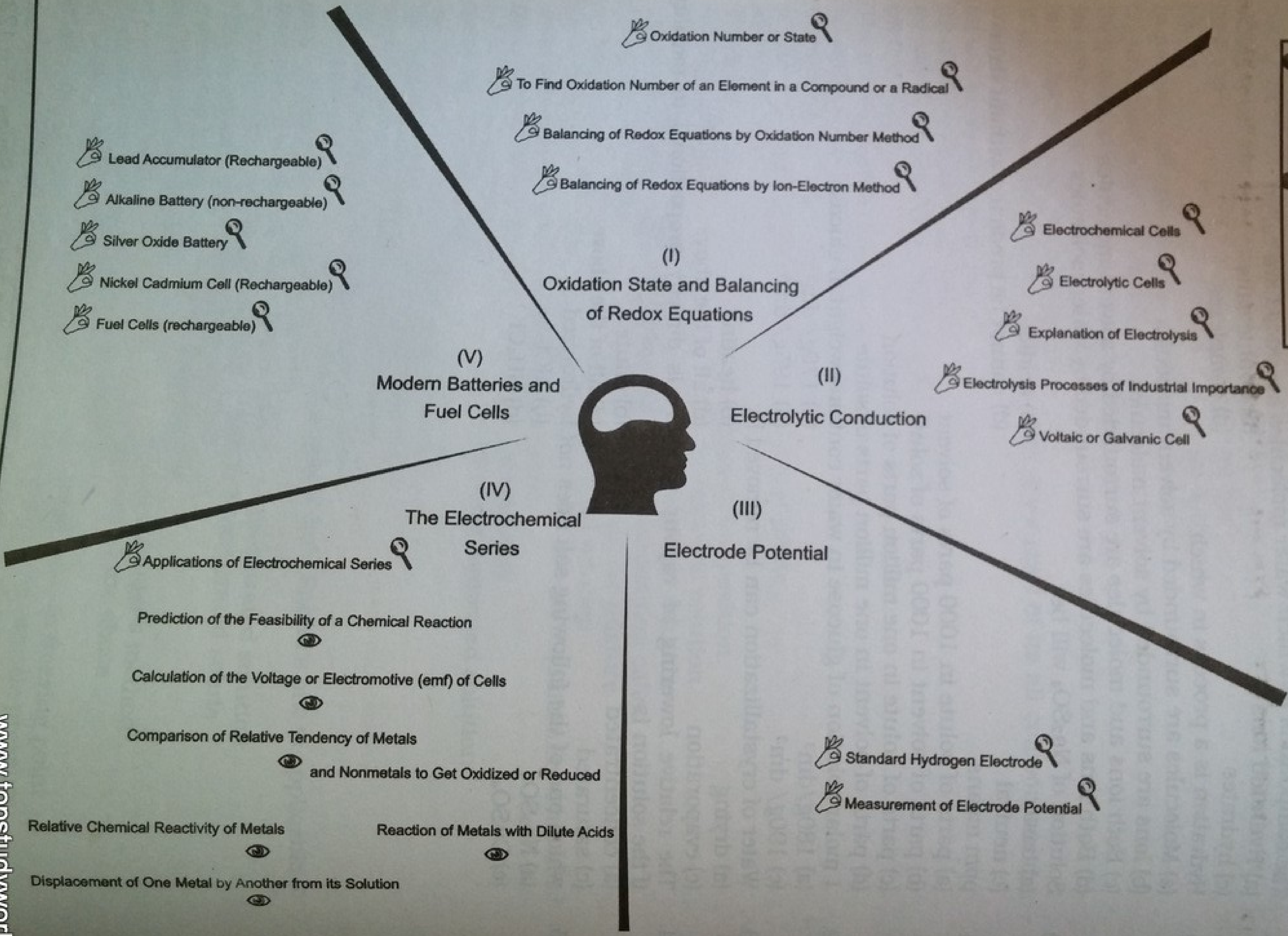
33. Water of crystallization can be removed by
(a) drying (b) heating
(c) evaporation (d) all of the above

34. The relative lowering of vapour pressure is directly proportional to molality if the solution is
(a) concentrated (b) dilute
(c) saturated (d) all of the above

35. which one of the following salt does not hydrolyzed
(a) Na_2SO_4 (b) $AlCl_3$
(c) $CuSO_4$ (d) NH_4Cl

Chapter 10

ELECTROCHEMISTRY



(I)
Oxidation State and Balancing of Redox Equations

- Oxidation Number or State
- To Find Oxidation Number of an Element in a Compound or a Radical
- Balancing of Redox Equations by Oxidation Number Method
- Balancing of Redox Equations by Ion-Electron Method

(II)
Electrolytic Conduction

- Electrochemical Cells
- Electrolytic Cells
- Explanation of Electrolysis
- Electrolysis Processes of Industrial Importance
- Voltaic or Galvanic Cell

(III)
Electrode Potential

- Standard Hydrogen Electrode
- Measurement of Electrode Potential

(IV)
The Electrochemical Series

- Applications of Electrochemical Series
  - Prediction of the Feasibility of a Chemical Reaction
  - Calculation of the Voltage or Electromotive (emf) of Cells
  - Comparison of Relative Tendency of Metals and Nonmetals to Get Oxidized or Reduced
  - Relative Chemical Reactivity of Metals
  - Reaction of Metals with Dilute Acids
  - Displacement of One Metal by Another from its Solution

(V)
Modern Batteries and Fuel Cells

- Lead Accumulator (Rechargeable)
- Alkaline Battery (non-rechargeable)
- Silver Oxide Battery
- Nickel Cadmium Cell (Rechargeable)
- Fuel Cells (rechargeable)

ELECTROCHEMISTRY

It is the branch of chemistry which is concerned with the inter-conversion of chemical energy and electrical energy.

- Electrical energy is converted into chemical energy through electrolytic cells.
- Chemical energy is converted into electrical energy through galvanic or voltaic cells.

OXIDATION STATE OR NUMBER

It is the apparent charge on an atom of an element in a molecule or an ion. It may be positive or negative or zero.

Rules for assigning oxidation number:

Element	• Molecular form • Bulk / chunk	H_2, S_8 0 Diamond (C) 0
Compound	• Covalent compound ➢ Molecular / Bulk / chunk *Non-Metal – Non-Metal* • Less electronegative non-metal = +ve • More electronegative non-metal = -ve • Algebraic sum of oxidation numbers = 0 • Ionic compound ➢ *Metal – Non-Metal* Metal = +ve Non-metal = –ve Algebraic sum of oxidation numbers = 0	Molecular HCl ; $(+1)+(-1)=0$ Bulk / chunk SiO_2 ; $[+4+2(-2)]=0$ Ionic compound NaCl $(+1)+(-1)=0$
Ion	• Mono-atomic ion ➢ Oxidation number will be equal to the charge on the ion. • Poly-atomic ion ➢ The algebraic sum of oxidation number is equal to charge on that ion.	Mono-atomic ion Cl^{-1} -1 Poly-atomic ion SO_4^{-2} $+6+[-2(4)]=$ -2
Hydrogen	• Ionic compound ➢ Always –ve oxidation number • Covalent compound ➢ Always +ve oxidation number	Ionic compound NaH $(+1)+(-1)=0$ Covalent compound H_2O $[+1(2)]+(-2)=0$
Oxygen	• With all elements. ➢ –2 oxidation number(normal oxides) ➢ –1 oxidation number(per oxides) ➢ –1/2 oxidation state (super oxides) • With Fluorine ➢ + 2 oxidation state	H_2O; $-1(2)-2=0$ H_2O_2; $+1-1=0$ KO_2; $[+1+2(-1/2)]=0$ OF_2; $[+2+2(-1)]=0$

Oxidation

- Gain in oxygen
- Loss of hydrogen
- Loss of electrons including anode reactions
- Increase in oxidation state

Reduction

- Loss in oxygen
- Gain of hydrogen
- Gain of electrons including cathode reactions
- Decrease in oxidation state

Oxidation number of IA group (+1)

Oxidation number of II-A group (+2)

Oxidation number of III-A group (+3)

Examples

$K_2Cr_2O_7$

$(+1)2+2Cr-2(7) = 0$

$+2+2Cr-14 = 0$

$2Cr =+14-2 = +12$

$Cr = +6$

$NaBrO_3$

$1+Br+(-2)(3) = 0$

$1+Br-6 = 0$

$Br = -5$

$Br = +5$

ELECTROLYTIC CONDUCTION

Electrolytic Conduction	Electronic Conduction
• Conduction through fused or aqueous electrolyte	• Conduction through solid metal
• It is due to mobile ions	• Due to free electrons
• Conduction increases with increase in temperature due to increase in ionization	• Conduction decreases with temperature due to increase in oscillations of cations

Products of electrolysis

(when electrodes take part in the reaction)

Electrolyte	Copper cathode	Copper anode
$CuSO_4$ (aq)	Cu deposits	Cu (s) dissolves to form Cu^{2+} ions
Electrolyte	Silver cathode	Silver anode
$AgNO_3$(aq) and HNO_3 (aq)	Ag deposits	Ag(s) dissolves to form Ag^+ ions

Products of electrolysis

(using inert electrodes of platinum or graphite)

Electrolyte	Cathode	Anode
$PbBr_2$(molten)	Pb(s)	Br_2(g)
NaCl (molten)	Na(s)	Cl_2(g)
NaCl (aq)	H_2 (g)	Cl_2(g)
$CuCl_2$ (aq)	Cu(s)	Cl_2(g)
$CuSO_4$ (aq)	Cu (s)	O_2 (g)
KNO_3 (aq)	H_2 (g)	O_2 (g)
NaOH (aq)	H_2 (g)	O_2 (g)
H_2SO_4 (aq)	H_2 (g)	O_2 (g)

USES OF ELECTROLYSIS

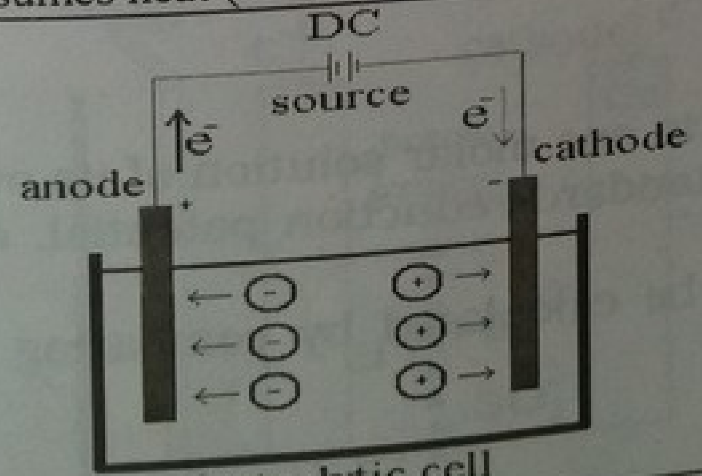
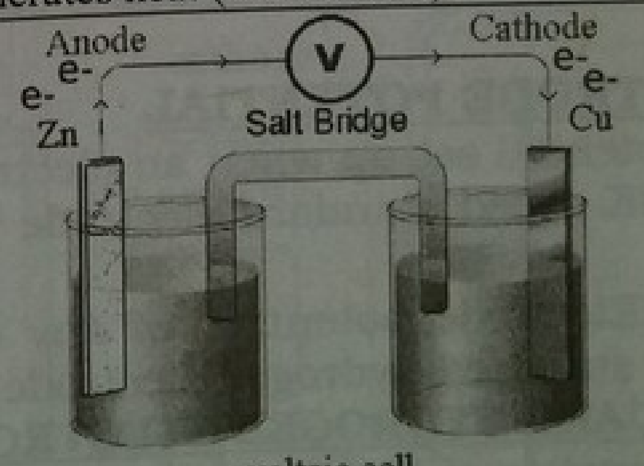
Particular	Description
Extraction of Na metal	Fused NaCl is used Down's cell is an example
Caustic soda from brine	Nelson cell (aqueous NaCl is used)
Mg and Ca extraction	Extraction occurs from their fused chlorides
Extraction of Al	Electrolysis of fused bauxite is conducted
Anodized Al	Prepared by making anode of Al
Purification of Cu	Anode is made up of impure copper
Electroplating	Copper, silver, nickel or chromium plating is done in electrolytic cell

ELECTROCHEMICAL CELLS

The cells consisting of electrodes dipped into an electrolyte which make the inter-conversion of electrical energy & chemical energy possible, are called electrochemical cells.

Types of electrochemical cells:

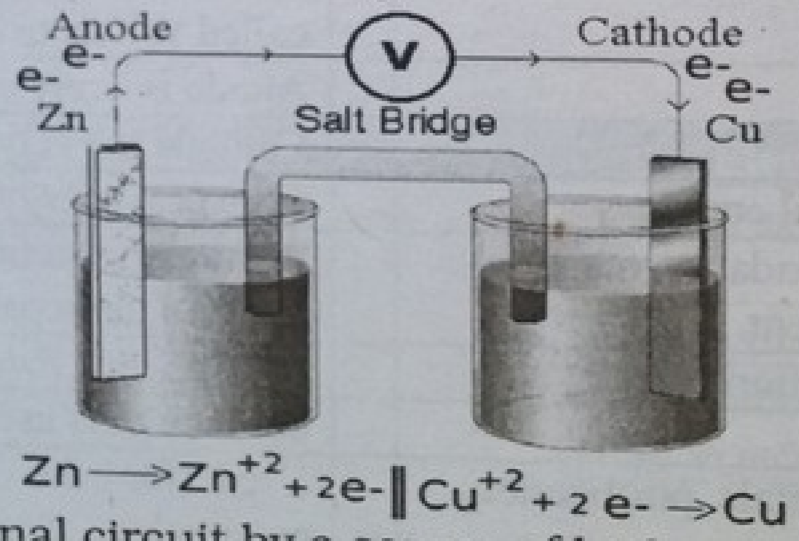
(i) Electrolytic cell:
(ii) Voltaic or galvanic cell:

Electrolytic Cell	Voltaic/Galvanic Cell
A cell in which a redox reaction occurs at the expense of electrical energy is called electrolytic cell.	A cell in which redox reaction generates electric current through chemical reaction is called voltaic or galvanic cell.
Anode is +vely charged	Anode is –vely charged.
Cathode is –vely charged.	Cathode is +vely charged.
Electrical energy → chemical energy	Chemical energy → electrical energy
Both reduction reaction & oxidation reaction occur in the same compartment.	Reduction reaction & oxidation reaction occur in the separate compartment.
Non-spontaneous redox reaction occurs.	Spontaneous redox reaction occurs.
Salt bridge is not used.	Salt bridge is used.
Used for the extraction of metals, purification, electroplating and anodizing.	Used for the measurement of electrode potential.
It consumes heat (endothermic)	It generates heat (exothermic)
 electrolytic cell	 Anode e- e- Zn V Salt Bridge Cathode e- e- Cu voltaic cell
Nelson's Cell & Down's Cell	Daniel's cell, Ni-Cd cell, fuel cell

VOLTAIC OR GALVANIC CELL

Two half cells are present in voltaic cell

- **Left Half Cell (Oxidation Half Cell)**
  Zn – electrode is dipped in 1M solution of $ZnSO_4$
- **Right Half Cell (Reduction Half Cell)**
  Cu – electrode is dipped in 1M solution of $CuSO_4$.
- **Salt Bridge**
  It is aqueous solution of KCl in a gel.
- **Working**
  - ➢ Connect both the half cells electrolytically through the salt bridge
  - ➢ Close the external circuit by connecting the Zn & Cu electrodes.
  - ➢ The electrons will flow from Zn to Cu through external circuit. The following reactions will occur at respective electrodes.
    - At anode
      $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$ oxidation
    - At cathode
      $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ reduction
    - The voltaic cell reaction is represented by
      $Zn^{(s)} / Zn^{2+}_{(aq)}\ 1M \parallel Cu^{2+}_{(aq)}\ 1M / Cu_{(s)}$
    - emf of the cell
      $E^0 = 1.10\ V$
- **Function of salt bridge**
  - ➢ Salt bridge acts as a passage for the transfer of negative ions (SO_4^{2-}) from right half-cell to left half-cell.
  - ➢ If the exchange of SO_4^{2-} ions is stopped, then the oxidation-reduction reaction will stop due to charge accumulation in both half cells



Replacing the external circuit by a source of high voltage can reverse the voltaic cell reactions. Such cell is called reversible cell.

ELECTRODE POTENTIAL

The potential set up when an electrode is dipped in one molar solution of its own ions at 298K called standard electrode potential or standard reduction potential, denoted by E.

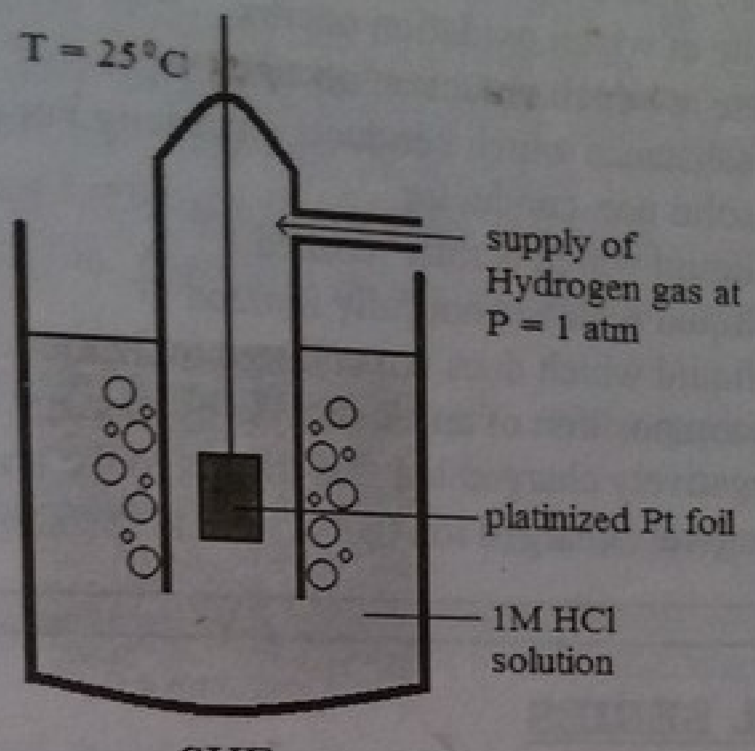
- Electrode potential, of any element, can be calculated by comparing it with standard hydrogen electrode (SHE.

STANDARD HYDROGEN ELECTRODE (SHE)

SHE consists of

- Glass Tube filled with H_2 gas at 1 atm. Pt–foil, coated with finally divided platinum black is suspended in it.

- The whole system mentioned above is dipped in 1M solution of HCl
- Electrode Potential of SHE is arbitrarily considered as zero



SHE

MEASUREMENT OF ELECTRODE POTENTIAL

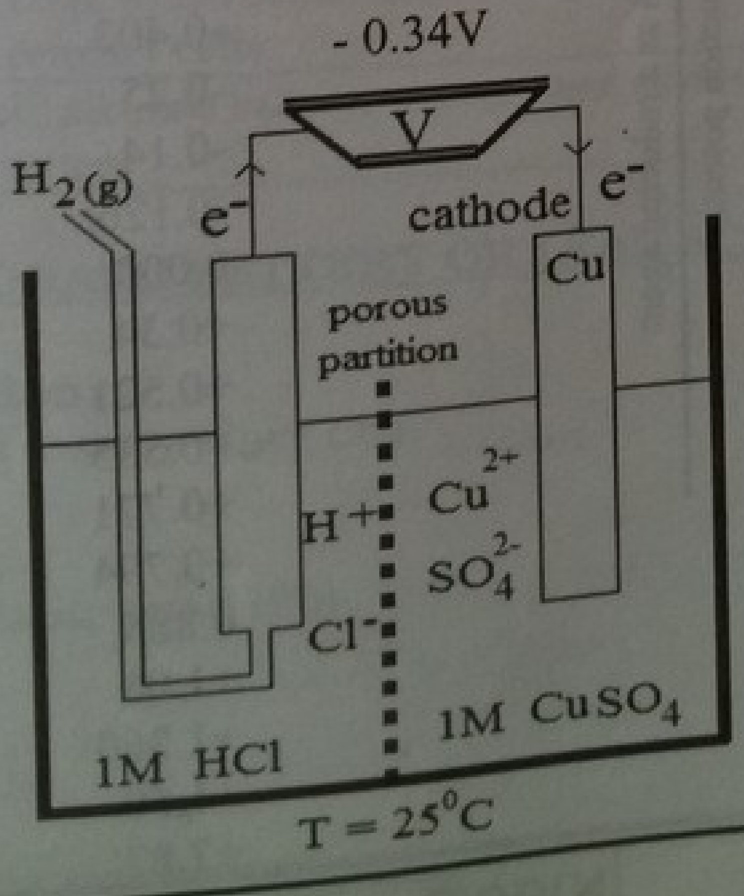
- Concerned electrode is joined with SHE and form a voltaic cell
- Salt bridge is used to connect both cells, filled with solution of KCl
- Voltmeter is attached to measure electrode potential
- Oxidation or Reduction occurs at SHE depending on the nature of the concerned electrode.
- When reduction occurs on SHE then volt meter reading will be +ve.

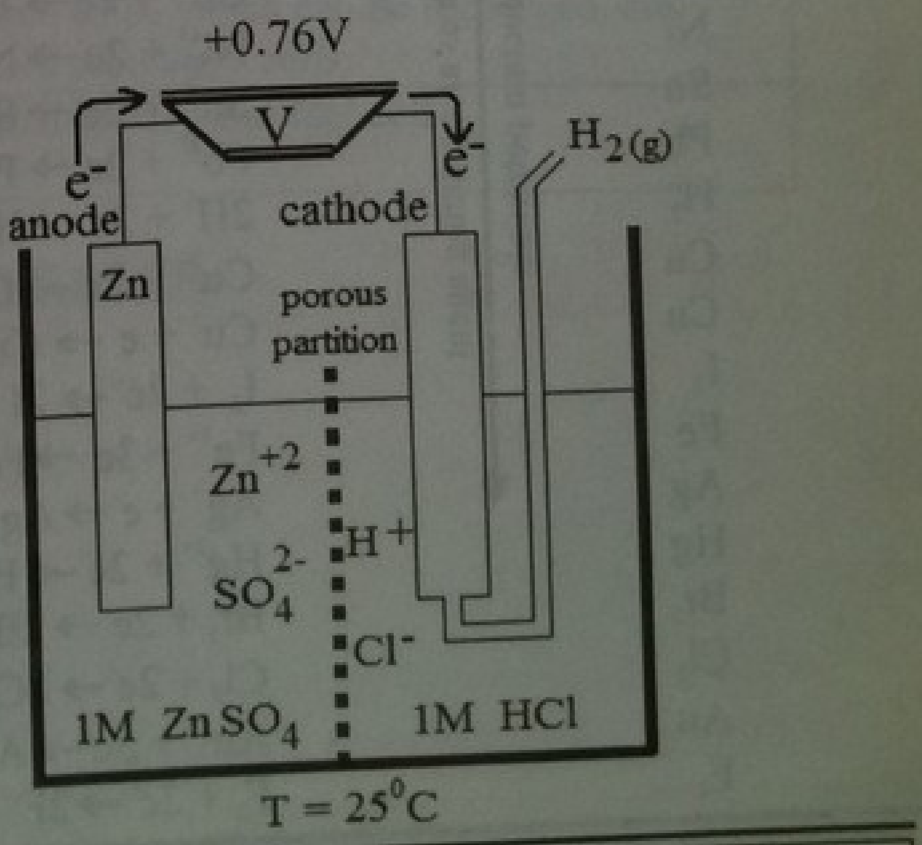
$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(gas)}$$

- When oxidation occurs on SHE then voltmeter reading will be in –ve

$$H_{2(gas)} \longrightarrow 2H^+_{(aq)} + 2e^-$$

- Potential of Zn is called oxidation potential
- Potential of Cu is called reduction potential





Electrode	Plate which carries electricity into the liquid
Anode	plate at which oxidation occurs
Cathode	plate at which reduction occurs
Conductor	A substance which conducts electricity but is not chemically changed
Insulator	A solid non-conductor
Strong electrolyte	A liquid which is fully ionized
Weak electrolyte	A liquid which is not fully ionized
Non-electrolyte	A liquid which does not undergo ionization.
Electrolysis	Decomposition of an electrolyte by passage of electricity
Anion	Negatively charged ion that travels to the anode during electrolysis
Cation	Positively charged ion that travels to the cathode during electrolysis

THE ELECTROCHEMICAL SERIES

When elements are arranged in the order of their increasing standard electrode potentials on the hydrogen scale, the resulting list is known as electrochemical series.

Electrochemical series

Element	Electrode	Standard Reduction Potential (E°)
Li	$Li^+ + e^- \rightarrow Li$	-3.045
K	$K^+ + e^- \rightarrow K$	-2.925
Ca	$Ca^{2+} + 2e^- \rightarrow Ca$	-2.87
Na	$Na^+ + e^- \rightarrow Na$	-2.714
Mg	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37
Al	$Al^{3+} + 3e^- \rightarrow Al$	-1.66
Zn	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76
Cr	$Cr^{3+} + 3e^- \rightarrow Cr$	-0.74
Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
Cd	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.403
Ni	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.25
Sn	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14
Pb	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.126
H_2	$2H^+ + 2e^- \rightarrow H_2$	0.000
Cu	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
Cu	$Cu^+ + e^- \rightarrow Cu$	+0.521
I_2	$I_2 + 2e^- \rightarrow 2I$	+0.535
Fe	$Fe^{3+} + 3e^- \rightarrow Fe$	+0.771
Ag	$Ag^+ + e^- \rightarrow Ag$	+0.794
Hg	$Hg^{2+} + 2e^- \rightarrow Hg$	0.885
Br_2	$Br_2 + 2e^- \rightarrow 2Br^-$	+1.08
Cl_2	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.360
Au	$Au^{3+} + 3e^- \rightarrow Au$	+1.50
F_2	$F_2 + 2e^- \rightarrow 2F^-$	+2.87

↓ Increasing strength as an oxidizing agent
Increasing reduction potentials

↑ Increasing strength as a reducing agent
decreasing reduction potentials

APPLICATIONS OF ELECTROCHEMICAL SERIES

Applications

(i) Prediction of the feasibility of a chemical reaction

The Electrochemical series tells us that whether a reaction is feasible or not. If the sum of E° values of the two half cell reaction is positive, the reaction is feasible and if it is negative then the reaction will not be feasible.

(ii) Calculation of the voltage or emf of the cell

- Electrode having higher position in series will act as an anode, oxidation will take place on it
- Electrode having lower position in series, will act as cathode, reduction will take place on it

(iii) Comparison of relative tendency of metals and non metals to get oxidized or reduced

- Value of the electrode potential shows, either the metal or non metal is oxidized or reduced

Greater value of standard reduction electrode potential greater will be the tendency to accept electron and undergo reduction and vice versa

(iv) Relative chemical reactivity of metals

Greater value of the standard reduction potential of a specie lesser will be its tendency to lose electron to form +ve ion hence lesser will be its reactivity.

(v) Reaction of metals with dilute acids

Greater the value of standard reduction potential of a metal, lesser its tendency to lose electrons to form metal ions and so weaker its tendency to displace H_2 from acids. For example Au, Pt, Ag and Cu do not liberate hydrogen from acids.

(vi) Displacement of one metal by another from its solution

Metal will displace another metal from the aqueous solution of its salt if it lies above the electrochemical series. For example Fe can displace Cu from $CuSO_4$. Zn does not displace Mg from solution of $MgSO_4$.

MODERN BATTERIES AND FUEL CELLS

Primary cells	Secondary cells:
Those cells which cannot be recharged are called primary cells.	Those cells, which can be recharged, are called secondary cells.
Dry cell, alkaline battery, mercury and silver oxide battery.	Ni-Cd-battery and fuel cells.

LEAD STORAGE BATTERY OR LEAD ACCUMULATOR

Introduction:

- ➢ It is a secondary cell.

Anode:

- ➢ Metallic Lead (Pb)

Cathode:

- ➢ PbO_2

Electrolyte:

- 30% H_2SO_4 having density $1.25g/dm^3$

Discharging:

- $Pb + PbO_2 + 4H^+ + 2SO_4^{-2} \longrightarrow 2PbSO_4 + 2H_2O$

Recharging:

- Anode and Cathode of the battery is connected to the anode & cathode of a source of high voltage.

$$2PbSO_4 + 2H_2O \longrightarrow Pb + PbO_2 + 4H^+ + 2SO_4^{-2}$$

Note:

- Concentration of H_2SO_4 decreases during discharging and it is restored on recharging.
- Density of H_2SO_4 decreases from $1.25g/dm^3$ to $1.15g/dm^3$ during discharging and it is restored on recharging.
- Lead Storage Battery consists of 6–cells and each cell produces energy of 2–volts.

Uses:

- It is used in car batteries

DIFFERENT BATTERIES

Particulars	Alkaline battery	AgO battery	Ni-Cd cell	Fuel cell
Type of cell	Primary	Primary	Secondary	Secondary
Anode	Zn rod	Zn metal	Cadmium	Porous carbon impregnated with Pt
Cathode	MnO_2	Ag_2O mixed with NaOH	NiO_2	Porous carbon impregnated with Pt
Nature of Electrolyte	Electrolyte is basic	Electrolyte is basic	Electrolyte is basic	KOH is electrolyte. It operates at high temperature.
Voltage	1.5V	1.5V	1.4V	75% bond energy into electricity
Uses	Toys, watches, tape recorder etc.	Battery, electronic watches, auto exposure camera	Mobile phones	Used in rocket as a fuel cell

Chapter 10

Electrochemistry

PRACTICE EXERCISE

30 mins
Time Yourself

1. Which of the following element act as inert electrode
(a) Cu (b) Ag
(c) Pt (d) None

2. If electricity is passed through $CuSO_4$ solution by using Pt electrode then which of the following possible change occurs?
(a) H_2 is deposited at cathode (b) Colour of the solution becomes fade
(c) Cu is deposited at anode (d) All are possible

3. Stronger the oxidizing agent, greater is the
(a) Oxidation potential (b) Reduction potential
(c) Redox potential (d) emf of cell

4. Which has maximum oxidation number?
(a) N (b) Cr
(c) S (d) Mn

5. Which of the following cell is not rechargeable?
(a) Lead storage battery (b) Silver oxide cell
(c) Fuel cell (d) Ni-Cd cell

6. In an electrolytic cell current flows?
(a) From cathode to anode in outer circuit
(b) From anode to cathode outside the cell
(c) From cathode to anode inside the cell
(d) both b & c

7. Which of the following is true in the case of Zn-Cu cell?
(a) The flow of electrons takes place from copper to zinc
(b) E^0_{red} of copper electrode is less than that of zinc electrode
(c) Zinc acts as an anode and copper as cathode
(d) All are correct

8. In a galvanic cell
(a) Chemical energy is converted into electricity
(b) Chemical energy is converted into heat
(c) Electrical energy is converted into chemical energy
(d) Electrical energy is converted into heat

9. The degree of dissociation of week electrolyte increases as
(a) Pressure increases (b) Dilution decreases
(c) Dilution increases (d) None

10. Molten NaCl conducts electricity due to the presence of
(a) Free electrons (b) Free molecules
(c) Free ions (d) Atoms of Na and Cl

11. In which of the following reactions, occur at cathode?
(a) $Cu^{2+} + 2e^- \rightarrow Cu$ (b) $Cu + 2e^- \rightarrow Cu^{2+}$
(c) $Hg + O_2 \rightarrow HgO$ (d) $Mg + O_2 \rightarrow MgO$

12. Electricity in voltaic cell is produced due to
(a) neutralization (b) oxidation
(c) reduction (d) both b & c

13. In electrolytic solution conductance of electricity is due to
(a) free electrons (b) ions
(c) metals (d) electrodes

14. In electrolytic cell, electricity carries
(a) spontaneous reaction (b) non-spontaneous reaction
(c) neutralization (d) all of above

15. Reaction at anode is called
(a) oxidation (b) reduction
(c) redox (d) decomposition

16. In an electrolytic cell cathode provides electrons to
(a) +ve ion (b) –ve ion
(c) neutral atom (d) does not provide any electron

17. In Galvanic cell, electrons flow from anode to cathode through
(a) external electric circuit (b) salt bridge
(c) movement of ions (d) all of the above

18. Decrease in oxidation number is called
(a) oxidation (b) reduction
(c) oxidation-reduction (d) all of above represent same entity

19. For the measurement of standard electrode potential, Zn is dipped in
(a) 1M ZnO solution (b) 1M $ZnSO_4$ solution
(c) 1.5M $ZnSO_4$ solution (d) 0.1M $ZnSO_4$ solution

20. Right half cell contains__________ electrode
(a) Al (b) Zn
(c) Cu (d) Fe

21. $Zn_{(s)}/Zn^{+2}_{(aq)}$ 1M || $Cu^{+2}_{(aq)}$ 1M/$Cu_{(s)}$ is representation of reaction in
(a) Daniel cell (b) Down's cell
(c) Voltaic cell (d) Nelson's cell

22. Salt bridge transfers
(a) electrons (b) anion
(c) current (d) ions

23. Voltaic cell can be recharged by
(a) by addition of fresh solution
(b) by replacing external circuit with external source of electricity
(c) by removal of solution
(d) by heating it

24. E^{o}_{red} of an element can be calculated by comparing it with
(a) New electrode of same element
(b) SHE
(c) 1M solution of ions of respective element
(d) 2M solution of HCl

25. Temperature for the measurement of standard electrode potential is
(a) 298K (b) 300K
(c) 30°C (d) 310K

26. H_2 gas in SHE is filled at pressure of
(a) 760mm of Hg (b) 750mm of Hg
(c) 780mm of Hg (d) 800mm of Hg

27. Potential of SHE is considered as
(a) zero (b) unity
(c) constant (d) multiple of 1

28. Chemical used in salt bridge is
(a) KOH (b) KCl
(c) KNO_3 (d) KBr

29. Electrode potential of Zn is
(a) oxidation
(b) reduction
(c) oxidation-reduction
(d) depends on the nature of the coupled electrode

30. List of elements based on hydrogen scale is called
(a) periodic table (b) groups
(c) periods (d) electrochemical series

31. The element that act as anode always have__________ position in electrochemical cell
(a) higher (b) lower
(c) in middle (d) no effect of position

32. In galvanic cell Zn acts as an anode so its value of standard reduction potentia in comparison to coupled electrode would be
(a) greater (b) lesser
(c) sum of reduction and oxidation potentials (d) none

33. Greater value of standard reduction potential greater will be tendency
(a) to get oxidized (b) To get reduced
(c) to accept electrons (d) both b and c

34. Greater value of standard reduction potential, smaller will be tendency
(a) to form positive ions (b) to form negative ions
(c) gain electrons (d) all are possible

35. Secondary cell is
(a) rechargeable (b) non rechargeable
(c) electrolytic cell (d) Daniel cell

36. Lead accumulators are
(a) secondary cell (b) primary cell
(c) voltaic cell (d) both a & c

37. Density of H_2SO_4 in lead accumulator is
(a) $1.25 g/cm^3$ (b) $1.3 g/cm^3$
(c) $1.20 g/cm^3$ (d) $1.15 g/cm^3$

38. Capacity of one lead accumulator cell is
(a) 1.5volts (b) 2 volts
(c) 3 volts (d) 1 volts

39. In alkaline battery, the anode is made up of
(a) MnO_2 (b) Zn
(c) AgO_2 (d) cadmium

40. The strength of solution of an element whose electrode potential is to be measured is
(a) 2M (b) 1N
(c) 1m (d) 1M

41. Apparent charge on atom in molecule is
(a) valency (b) coordination number
(c) oxidation number (d) charge number

42. Voltaic cell is a
(a) irreversible cell (b) reversible cell
(c) alkaline cell (d) all of the above

43. In $K_2Cr_2O_7$, the oxidation number of chromium is
(a) +7 (b) +6
(c) -7 (d) -6

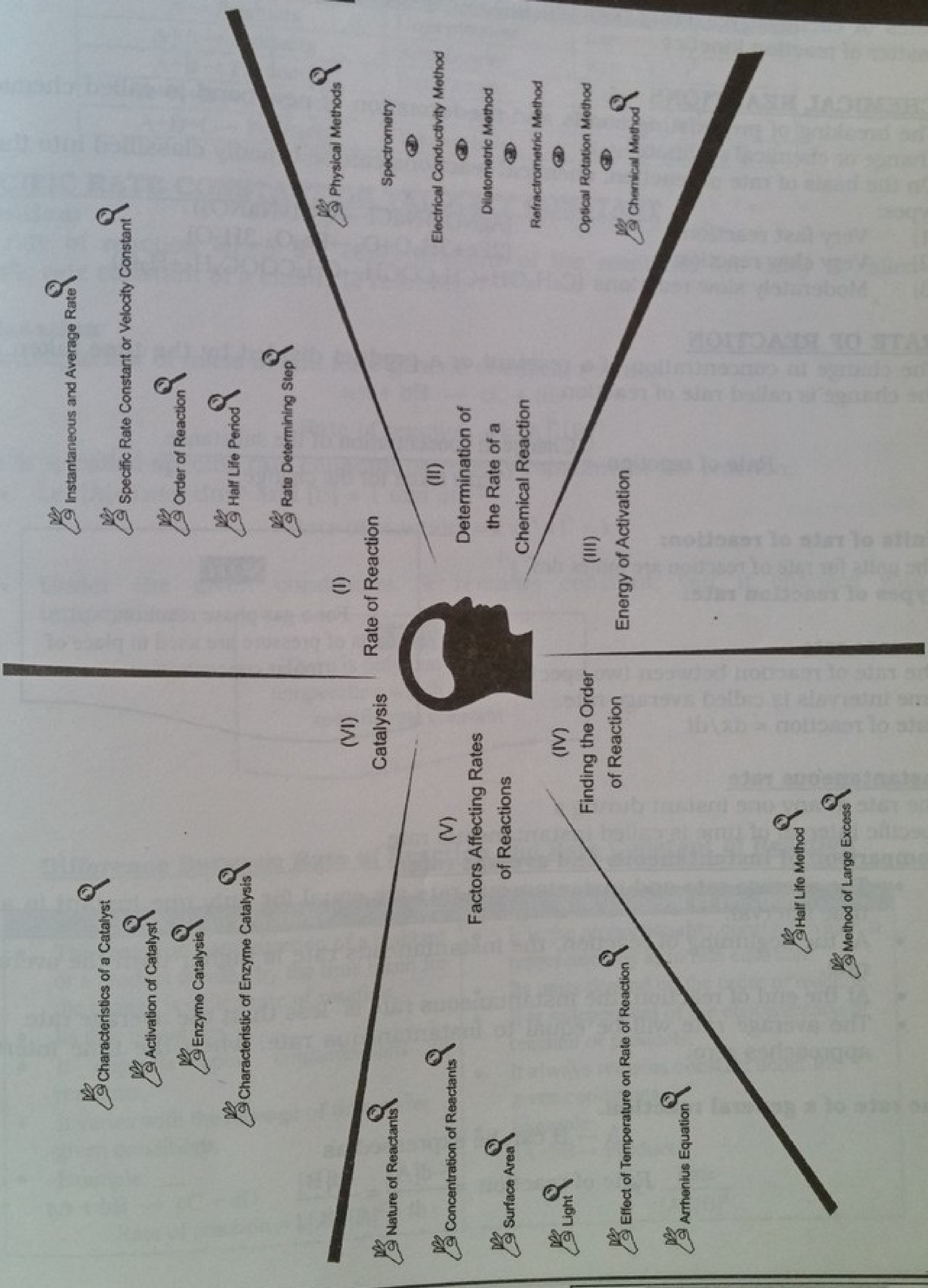
44. Percentage of sulphuric acid in lead accumulator is
(a) 40% (b) 25%
(c) 30% (d) 50%

45. The reduction potential of Zn is
(a) 0.76 (b) –0.76
(c) –0.55 (d) 0.55

46. The half cells are interconnected through
(a) wire (b) salt bridge
(c) electric circuit (d) no connection exists

Chapter 11

CHEMICAL KINETICS


(I) Rate of Reaction
Instantaneous and Average Rate
Specific Rate Constant or Velocity Constant
Order of Reaction
Half Life Period
Rate Determining Step
(II) Determination of the Rate of a Chemical Reaction
Physical Methods
Spectrometry
Electrical Conductivity Method
Dilatometric Method
Refractrometric Method
Optical Rotation Method
Chemical Method
(III) Energy of Activation
(IV) Finding the Order of Reaction
Half Life Method
Method of Large Excess
(V) Factors Affecting Rates of Reactions
Nature of Reactants
Concentration of Reactants
Surface Area
Light
Effect of Temperature on Rate of Reaction
Arrhenius Equation
(VI) Catalysis
Characteristics of a Catalyst
Activation of Catalyst
Enzyme Catalysis
Characteristic of Enzyme Catalysis

Chapter 11 Chemical Kinetics

REACTION KINETICS

The studies concerned with rates of chemical reactions and factors that affect the rates of chemical reactions and the mechanism of reactions constitute the subject matter of reaction kinetics

CHEMICAL REACTIONS

The breaking of pre-existing bonds and the formation of new bond is called chemical change or chemical reaction.

On the basis of rate of reaction, chemical reactions can be broadly classified into three types;

(1) Very fast reaction ($AgNO_3+NaCl \rightarrow AgCl+NaNO_3$)
(2) Very slow reaction ($2Fe+3H_2O+O_2 \rightarrow Fe_2O_3.3H_2O$)
(3) Moderately slow reactions ($C_2H_5OH+CH_3COOH \rightarrow CH_3COOC_2H_5+H_2O$)

RATE OF REACTION

The change in concentration of a reactant or a product divided by the time taken for the change is called rate of reaction.

$$\text{Rate of reaction} = \frac{\text{Change in concentration of the substance}}{\text{Time taken for the change}}$$

Units of rate of reaction:

The units for rate of reaction are moles $dm^{-3}s^{-1}$

Types of reaction rate:

Average rate

The rate of reaction between two specific time intervals is called average rate.

Rate of reaction = dx/dt

NOTE

For a gas phase reaction, units of pressure are used in place of molar concentration.

Instantaneous rate

The rate at any one instant during a specific interval of time is called instantaneous rate.

Comparison of instantaneous and average rate:

- The average rate and instantaneous rate are equal for only one instant in any time interval.
- At the beginning of reaction, the instantaneous rate is higher than the average rate.
- At the end of reaction, the instantaneous rate is less than the average rate
- The average rate will be equal to instantaneous rate, when the time interval approaches zero.

The rate of a general reaction.

$A \rightarrow B$ can be expressed as

$$\text{Rate of reaction} = \frac{-d[A]}{dt} = \frac{+d[B]}{dt}$$

Chapter 11

Chemical Kinetics

RATE LAWS FOR ELEMENTARY REACTIONS

Elementary Reaction	Molecularity	Rate Law
A→ Products	Unimolecular	Rate = k [A]
A+A→ Products	Bimolecular	Rate = $k[A]^2$
A+B→ Products	Bimolecular	Rate = k [A][B]
A+A+B→ Products	Termolecular	Rate = $k[A]^2[B]$
A+B+C→ Products	Termolecular	Rate = k[A][B][C]

SPECIFIC RATE CONSTANT OR VELOCITY CONSTANT

Definition:

The rate of reaction when the concentrations of the reactants are unity is called specific rate constant of a chemical reaction.

Explanation

According to law of mass action for a general chemical reaction.

$$aA + bB \rightarrow cC + dD$$

$$\text{Rate of reaction} = k[A]^a[B]^b$$

Here 'k' is called specific rate constant or velocity constant for the reaction.

- Let $[A] = 1\text{mol dm}^{-3}$ and $[B] = 1\text{ mol dm}^{-3}$

$$\text{Rate of reaction} = k \times 1^a \times 1^b = k$$

- Under the given conditions, k remains constant, but it changes with temperature.

NOTE

There is only one factor i.e. temperature which affects the specific rate constant

Difference Between Rate of Reaction and Rate Constant of Reaction

Rate of reaction	Rate constant of reaction
• The change in concentration of a reactant or a product divided by the time taken for the change is called rate of reaction. • Its unit is mol $dm^{-3}s^{-1}$. • It depends upon concentrations of reactants. • It varies with the passage of time under given conditions. • Example: $aA + bB \rightarrow cC + dD$ Rate of reaction = $k[A]^a[B]^b$	• It is the proportionality constant, which is represented by k, in rate equation. • Its units depend on the order of reaction. • It is independent of the concentration of reactant or products. • It always remains constant under the given conditions. • Example: $aA+bB \rightarrow$ Product $k = \dfrac{\text{Rate}}{[A]^a[B]^b}$

RATE DETERMINING STEP

When the reaction completes in more than one step, then the slowest step will give the overall rate of reaction, thus slowest step of such a reaction is called rate determining step.

DETERMINATION OF RATE OF REACTION

- Determination of rate of reaction involves the measurement of concentration of reactants.
- Graph is plotted between concentration of reactant and time & we get a curve.
- Select any two points in a curve.
- Make a right angle triangle of these points.
- Getting the tanθ of right angle triangle, we shall get

$$\text{Rate of reaction} = \frac{\text{Change in concentration of reactant}}{\text{Change in time}}$$

METHODS FOR THE DETERMINATION OF RATE OF A CHEMICAL EACTION

Physical Methods

Techniques	Details
Spectrometry	▪ Spectrophotometer is used. ▪ Reactants and products absorbs U.V, I.R radiations ▪ Amount of radiation absorbed give rate of reaction
Electrical conductive method	▪ Conductometer is used ▪ Conductivity depends on the concentration of ions in the solution. ▪ Conductivity of ions of reactants give rate of reaction
Dilatometric method	▪ It is applied to the reaction in which volume of solution is changed. ▪ Volume change of a reaction is proportional to extent of reaction.
Optical rotation method	▪ Polarimeter is used ▪ Reacting molecules rotates angle of rotation of plane of polarized light ▪ Value of angle of rotation gives information about rate of reaction
Refractometric method	▪ Refractometer is used ▪ It is applied to the reaction in which change in refractive indices occurs. ▪ Transformation of glucose into alcohol can be analyzed regarding rate of reaction through this method

Chemical Method

- Titration

FACTORS AFFECTING THE RATE OF REACTION

Name	Details
Nature of reactant	▪ More active reactants give fast rate of reaction ▪ No. of electrons present in innermost shell affects the reactivity of reactant ▪ Elements of IA are more reactive than IIA. ▪ Neutralization reactions and decomposition reactions are very fast. ▪ Oxidation reduction reactions are slower ▪ Ionic reactions are very fast
Concentration of reactant	▪ Reaction is due to effective collision of reactant molecules. ▪ Greater concentration of reactants, more effective collisions, thus rate of reaction will be high ▪ In case of reactants in gases, their concentration is increased by increasing their partial pressures ▪ Rate of reaction is directly proportional to concentration of reactants ▪ Sometime concentration of reactant become double and rate of reaction increases four times
Surface area	▪ Greater the surface area, greater will be chance of contact of molecules ▪ Greater surface area of molecules, greater will be rate of reaction.
Light	▪ Light travel in the form of photons. ▪ Photons have energy depending on frequency of light. ▪ Light gives the energy to reactants to form activated complex in minimum time. ▪ Light increases the rate of reaction.
Temperature	▪ By increasing temperature, the number of collisions of molecule increases ▪ Rate of reaction increases by increase in temperature of reaction ▪ On increasing temperature by 10K, the rate of reaction becomes doubled. ▪ Arrhenius equation: $K = Ae^{-Ea/RT}$ (it gives us the quantitative effect of temperature on rate of reaction.

ORDER OF REACTION

The sum of all the exponents to which the concentrations in the rate equation are raised is called order of reaction.

OR

The number of reacting molecules, whose concentration alter as a result of the chemical change, is called order of reaction.

$$aA + bB \longrightarrow P$$

$$\frac{dx}{dt} = k[A]^a[B]^b$$

Order of reaction = a+b

IMPORTANT POINTS

- The order of a reaction is an experimentally determined quantity and cannot be inferred simply by looking at the reaction equation.
- The sum of the exponents in the rate equation may or may not be the same as in a balanced chemical equation.

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- The order of reaction provides valuable information about the mechanism of a reaction.
- Maximum order of reaction is three
- Order of reaction can be zero or can be in fraction
- Order of reaction is related with rate equation and is controlled by rate law.
- Order of reaction help us determine mechanism of reaction
- If the molecularity and order of reaction is same then it is said to be a simple reaction. Otherwise it is complex reaction.

The chemical reactions are classified as;

- Zero order reaction
- First order reaction
- Second order reaction
- Third order reaction
- Pseudo first order reaction
- Fractional order reaction

EXAMPLES OF ORDER OF REACTIONS

Zero order reactions

Photochemical reactions are usually zero order.

First order reaction

$N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$

Second order reactions

(i) $2CH_3CHO \rightarrow 2CH_4 + 2CO$
(ii) $NO + O_3 \rightarrow NO_2 + O_2$

Third order reactions

(i) $SnCl_2 + 2FeCl_3 \rightarrow SnCl_4 + 2FeCl_2$
(ii) $2NO + Cl_2 \rightarrow 2NOCl$

HALF LIFE PERIOD

The time required to convert 50% of the reactants into products is called half-life period.

Example

(i) Half-life period of N_2O_4 at 45°C is 24 minutes.
(ii) Half-life period of $^{235}_{92}U$ is 7.1×10^8 or 710 million years.

MPORTANT POINTS

- Half-life period of second order reaction is inversely proportional to the initial concentration of the reactants.
- Half-life period of third order reaction is inversely proportional to the square of initial concentration of reactants.

In general for the reaction of nth order:

$$\left[t_{1/2}\right]_n \propto \frac{1}{a^{n-1}}$$

Chapter 11

Chemical Kinetics

METHODS TO DETERMINE THE ORDER OF REACTION

Five methods are available.

(i) Method of hit and trail
(ii) Graphical method
(iii) Differential method
(iv) Half life method
(v) Method of large excess

ENERGY OF ACTIVATION

The minimum amount of energy, in addition to the average kinetic energy, which the particles must have for effective collisions, is called activation energy.

IMPORTANT POINTS

- Reactants go into transition state before going into product called activated complex.
- Energy of activated complex is higher than reactants and products.
- Amount of energy to form transition state is called energy of activation.
- Effective collision produces products.
- In effective collision, molecules have certain amount of energy and collide in certain orientation.
- When the energy of products is lesser than reactants, the reaction is exothermic.
- When the energy of products is higher than reactants, the reaction is endothermic.
- Energy of activation of forward reaction is less than backward reaction for an exothermic reaction.
- Energy of activation for backward reaction is less than forward reaction for an endothermic reaction.

ARRHENIUS EQUATION

According to Arrhenius

$K = Ae^{-Ea/RT}$

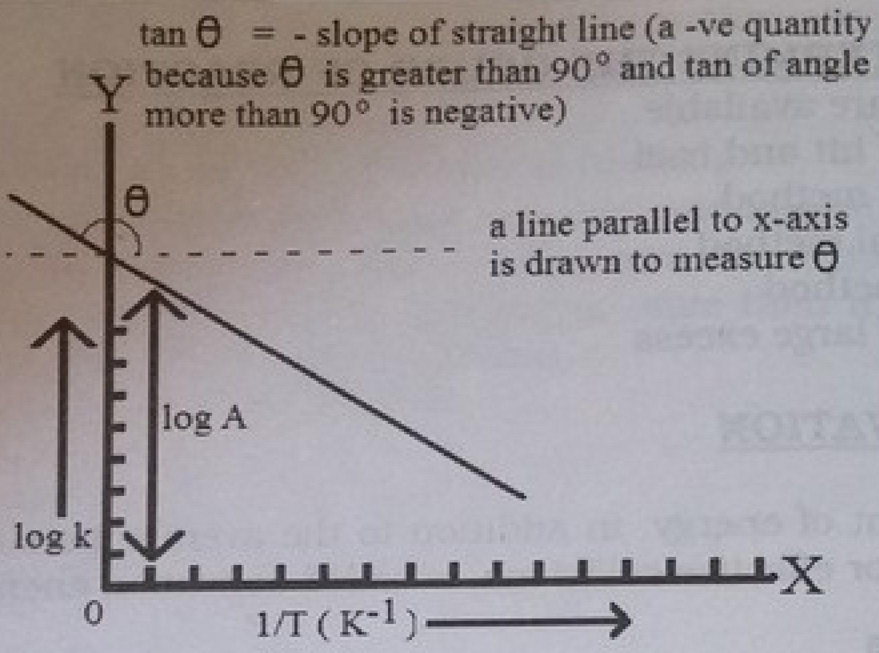
In this equation

K = specific rate constant
A = Arrhenius constant.

It tells us about collision frequency.

Points to be remembered:

- This equation explains the effect of temperature on the rate constant of reaction.
- k is exponentially related to activation energy and temperature.
- When a graph is plotted between $\frac{1}{T}$ on x-axis and log k at y-axis, a straight line is obtained with a negative slope. Actually, $\frac{E_a}{RT}$ has negative sign so the straight line has two ends in second and fourth quadrants.



- $Slope = \frac{-E_a}{2.303R}$ Unit of slope is Kelvin
- This equation helps us to determine activation energy of the reaction.
- E_a = -Slope x 2.303R
- Unit of activation energy is Joule mole^{-1}, greater is value of activation energy smaller is k value hence smaller will be the rate

CATALYST

A substance, which alters the rate of a chemical reaction, but remains chemically unchanged at the end of the reaction, is called catalyst.

CATALYSIS

The process, which takes place in the presence of a catalyst, is called catalysis.

Types of Catalysis

1- **Homogeneous catalysis**

In this type of catalysis, the catalyst and the reactants are in the same phase and the reacting system is homogenous throughout.

Examples

$$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{NO(g)} 2SO_{3(g)}$$

$$CH_3COOH_{(aq)} + C_2H_5OH_{(aq)} \xrightleftharpoons{H+} CH_3COOC_2H_{5(aq)} + H_2O_{(\ell)}$$

2- **Heterogeneous catalysis**

When the phase of catalyst differ from phase of reactant, catalysis is called heterogeneous catalysis.

Example

$$4NH_{3(g)} + 5O_{2(g)} \xrightleftharpoons{Pt(s)} 4NO_{(g)} + 6H_2O_{(g)}$$

CHARACTERISTICS OF A CATALYST

- Catalyst remains chemically unchanged.
- Catalyst is more effective when it is in finely divided powder form.
- Catalyst should not affect chemical equilibrium state of reaction.
- Catalyst cannot start a reaction; it only lowers the energy of activation.
- Catalysts are specific in their nature.
- Catalytic poisoning occurs when any foreign particle affect the activity of catalyst.
- Addition of impurity in catalyst is called poisoning of catalyst.

  It may be
    - Permanent poisoning
    - Temporary poisoning

Examples

- HCl can poison Pt in decomposition of H_2O_2.
- CO in Haber's Process can poison V_2O_5/Pt.

ACTIVATION OF CATALYST

Promoter

Substance that increases the activity of catalyst is called promoter or activators or catalyst of the catalyst.

Example

Cu promotes activity of Ni in hydrogenation of oil.

Inhibitor

When a substance reduces the rate of reaction then it is called inhibitor or negative catalyst.

Example

Tetraethyl lead is added to petrol which acts as inhibitor or negative catalyst.

Autocatalyst

In some reactions, products formed act as catalyst called autocatalysis.

Examples

- Hydrolysis of ester gives acetic acid which act as catalyst.
- The reaction of oxalic acid with acidified $KMnO_4$, $MnSO_4$ is produced Mn^{+2} ions act as auto catalyst.

ENZYME CATALYSIS

Enzymes are biocatalytical proteins, which increase the rate of biochemical reactions.

- The substance on which an enzyme can attack is called substrate.
- The point through which an enzyme attacks on substrate called active site.
- Each enzyme has its own active site.
- Enzymes are highly specific for substrate.
- Enzyme and substrate forms enzyme-substrate complex, which then breaks into product and enzyme.
- The name of enzyme usually ends on "ase".

Examples

Urease, Zymase, Dehydrogenase, Hydrolase, Maltase

CHARACTERISTICS OF ENZYME CATALYSIS

- The catalytic activity of enzymes is greatly enhanced by the presence of a co-enzyme or activator
- Enzyme catalysis is highly specific e.g. urease catalyses the hydrolysis of urea only and it cannot hydrolyse any other amide even methyl urea.
- Enzyme catalytic reactions have the maximum rates at an optimum temperature.
- The pH of the system also controls the rates of the enzyme catalysed reaction
- and the rate passes through a maximum at a particular pH, known as an optimum pH. The activity of enzyme catalyst is inhibited by a poison.

Chapter 11

Chemical Kinetics

PRACTICE EXERCISE

30 mins Time Yourself

1. The rate of reaction
(a) Increases as the reaction proceeds.
(b) Decreases as the reaction proceeds.
(c) Remains the same as the reaction proceeds.
(d) May decrease or increase as the reaction proceeds.

2. The addition of a catalyst to the reaction system.
(a) Increases the rate of forward reaction only.
(b) Increases the rate of reverse reaction.
(c) Increases the rate of forward but decreases the rate of backward reaction.
(d) Increases the rate of forward as well as backward reaction equally.

3. The specific rate constant of a first order reaction depends on the
(a) Time
(b) Concentration of the reactant
(c) Temperature
(d) Concentration of the product.

4. On increasing the temperature, the rate of reaction increases mainly because
(a) The activation energy of the reaction increases
(b) Concentration of the reacting molecules increases
(c) Collision frequency increases
(d) None of these

5. $-d[N_2O_5]/dt$ represents
(a) Rate of formation of N_2O_5
(b) Rate of decomposition of N_2O_5
(c) Order of the reaction
(d) None.

6. The value of activation energy is primarily determined by
(a) Temperature
(b) Effective collision
(c) Concentration of reactants
(d) Chemical nature of reactants and products

7. Sum of exponents of molar concentration is called
(a) Order of reaction
(b) Molecularity
(c) Rate of reaction
(d) Average of reaction

8. Spontaneous reactions are
(a) Moderate
(b) Slow
(c) Fast
(d) not natural

9. In rate expression, the concentration of reactants is negative. It shows
(a) Concentration of reactant does not change
(b) Concentration of product increases
(c) Concentration of reactant decreases
(d) Concentration of reactant increases

10. Unit of rate of reaction is
(a) Moles dm^{-3} sec^{-1}
(b) Moles dm^{-3}
(c) Moles sec^{-1}
(d) Mol^{-1} dm^{3} sec^{-1}

11. When a graph is plotted between $\frac{1}{T}$ on x-axis and log k on y-axis a straight line is obtained with a negative slope which has two end in
(a) I and II quadrant
(b) II and III quadrant
(c) III and IV quadrant
(d) II and IV quadrant

12. Rate of disappearance of reactant is equal to
(a) Rate of reaction
(b) Rate of formation of product
(c) Energy released during reaction
(d) a and b

13. Rate of reaction, when concentration of reactants are taken as unity is called
(a) Arrhenius constant
(b) Molecularity
(c) Specific rate constant
(d) Ideal rate constant

14. Order of reaction of $2N_2O_5 \rightarrow 2N_2O_4 + O_2$ is
(a) First order
(b) Second order
(c) Third order
(d) Zero order

15. For 3rd order reaction, the half life is inversely proportional to initial concentration of reactants
(a) Single
(b) Square
(c) Cube
(d) Raise to power four

16. Which order of reaction obeys the relation $t_{1/2} = 1/Ka$
(a) First order
(b) Second order
(c) Third order
(d) Zero order

17. Radiations are absorbed in
(a) Spectrophotometer method
(b) Dilatometric method
(c) Optical relation method
(d) Refractometric method

18. Activated complex is formed due to
(a) Pressure
(b) Effective collisions
(c) Ineffective collisions
(d) Temperature

19. Energy of reactant higher than energy of product favours
(a) Endothermic
(b) Exothermic
(c) Moderate reaction
(d) No reaction

20. Energy required to form transition state is called
(a) Ea
(b) P.E
(c) V
(d) K.E

21. Which of the following will have very high rate of reaction?
(a) Double decomposition reaction
(b) Neutralization reaction
(c) Ionic reactions
(d) all of above

22. Greater the conc. of reactant
(a) Greater will be dx/dt
(b) Lesser will be dx/dt
(c) dx/dt will be moderate
(d) any of above

23. Anything which increases rate of reaction without being involved in the reaction.
(a) Promoter
(b) Catalyst
(c) Inhibitor
(d) All of the above

24. The substances that reduces the effectiveness of a catalyst are called
(a) Promoters
(b) Poisoning catalysts
(c) Inhibitors
(d) pro-catalysts

25. When catalysts and reactants are in more than one phase, it is
(a) Homogeneous catalysis
(b) Heterogeneous catalysis
(c) Catalysis
(d) Ea

26. Each catalyst has
(a) Specificity
(b) Special structure
(c) Its own Ea
(d) All of above

27. Biocatalytical proteins are
(a) Enzymes
(b) Substrate
(c) Lipids
(d) Any of above

28. A catalyst can not effect
(a) Products (b) Chemical equilibrium
(c) Reactants (d) both a & b

29. An enzyme has its specificity due to
(a) Substrate (b) Structure
(c) Temperature (d) Pressure

30. Co-enzymes are
(a) Non proteineous (b) Proteineous
(c) sugars (d) lipids

31. A substance which increases the reactivity of enzyme is called
(a) Promoters (b) Inhibitors
(c) Stimulators (d) Non-activators

32. Addition of tetraethyl lead in petrol is example of
(a) +ve catalysis (b) –ve catalysis
(c) auto catalysis (d) anti catalysis

33. When a product acts as catalyst then it is called
(a) Autocatalysis (b) –ve catalysis
(c) +ve catalysis (d) self catalysis

34. End name of enzyme is
(a) yl (b) ase
(c) one (d) al

35. When the reaction completes in more than one steps, rate of reaction will be determined by
(a) Fast step (b) Slowest step
(c) All steps (d) Molecularity of the reaction

36. For determining the order of reaction, we use
(a) Refractometric method (b) Dilatometric method
(c) Optical activity method (d) Half life method

37. Energy of activation for backward reaction is less than forward reaction for__________ reaction
(a) Endothermic (b) Exothermic
(c) Moderate (d) Fast

38. The unit of slope in Arrhenius plot to calculate the energy of activation is
(a) K^{-1} (b) °F
(c) K (d) °C

39. Which statement is incorrect about catalyst
(a) it is used in smaller amount (b) decrease activation energy
(c) specific in action (d) it affects specific rate constant

40. Which of the following type of reaction is 3rd order reaction
(a) $2N_2O_5 \rightleftharpoons 2N_2O_4 + O_3$ (b) $NO + O_3 \longrightarrow NO_2 + O_2$
(c) $2FeCl_3 + 6KI \longrightarrow 2FeI_2 + 6KCl + I_2$ (d) none of these

ANSWER KEY

KIPS DIAGNOSTIC TEST

1	D	11	C	21	B	31	B	41	A	51	C
2	B	12	A	22	A	32	C	42	D	52	D
3	D	13	C	23	C	33	C	43	C	53	C
4	D	14	D	24	C	34	B	44	B	54	C
5	C	15	C	25	B	35	B	45	D	55	B
6	B	16	C	26	D	36	D	46	C	56	C
7	D	17	D	27	A	37	A	47	B	57	C
8	D	18	C	28	D	38	B	48	A	58	B
9	D	19	C	29	C	39	B	49	B	59	C
10	D	20	A	30	D	40	C	50	C	60	A

CHAPTER-1

1	C	11	A	21	A	31	D
2	D	12	D	22	C	32	A
3	B	13	D	23	B	33	C
4	D	14	C	24	D	34	C
5	C	15	C	25	C	35	A
6	D	16	C	26	A	36	D
7	D	17	A	27	C	37	D
8	D	18	A	28	A	38	A
9	A	19	C	29	C	39	C
10	C	20	B	30	A	40	A

CHAPTER-2

1	A	11	A	21	D	31	B
2	D	12	C	22	A	32	B
3	C	13	B	23	C	33	C
4	B	14	B	24	C	34	B
5	B	15	C	25	B	35	D
6	C	16	B	26	B	36	C
7	B	17	B	27	A	37	A
8	C	18	B	28	B	38	A
9	C	19	D	29	B	39	B
10	B	20	B	30	B	40	C

CHAPTER-3

1	A	11	D	21	B	31	D
2	B	12	B	22	B	32	B
3	A	13	D	23	C	33	A
4	B	14	A	24	C	34	B
5	C	15	D	25	A	35	A
6	D	16	B	26	C	36	C
7	D	17	A	27	B	37	D
8	D	18	C	28	D	38	C
9	C	19	A	29	A	39	D
10	B	20	C	30	A	40	D

CHAPTER-4

1	C	11	D	21	A	31	B	41	B
2	D	12	C	22	B	32	B	42	B
3	B	13	C	23	A	33	D	43	C
4	A	14	B	24	C	34	B	44	B
5	A	15	A	25	B	35	C	45	D
6	C	16	B	26	B	36	A	46	D
7	B	17	C	27	B	37	B	47	C
8	D	18	D	28	D	38	B	48	B
9	B	19	B	29	A	39	B	49	C
10	B	20	C	30	A	40	A	50	C

CHAPTER-5

1	D	11	B	21	B	31	C	41	B
2	B	12	D	22	D	32	D	42	C
3	B	13	C	23	C	33	A	43	C
4	A	14	A	24	D	34	B	44	A
5	C	15	A	25	B	35	C	45	A
6	B	16	B	26	B	36	C	46	C
7	B	17	B	27	B	37	A	47	A
8	D	18	D	28	D	38	B	48	A
9	D	19	C	29	C	39	A	49	B
10	C	20	D	30	D	40	A	50	C

CHAPTER-6

1	C	11	C	21	B	31	B	41	B
2	A	12	B	22	D	32	B	42	B
3	B	13	B	23	A	33	B	43	A
4	C	14	D	24	A	34	A	44	A
5	D	15	D	25	A	35	A	45	C
6	A	16	B	26	B	36	D	46	B
7	B	17	D	27	B	37	B	47	B
8	C	18	A	28	C	38	D	48	C
9	C	19	A	29	A	39	A	49	D
10	B	20	B	30	C	40	B	50	A

CHAPTER-7

1	D	11	B	21	D
2	A	12	D	22	A
3	D	13	A	23	A
4	B	14	B	24	A
5	D	15	D	25	C
6	A	16	D	26	B
7	C	17	D	27	C
8	A	18	A	28	B
9	C	19	B	29	A
10	A	20	A	30	D

CHAPTER-8

1	B	11	D	21	D	31	A
2	C	12	C	22	A	32	B
3	D	13	D	23	A	33	B
4	C	14	A	24	B	34	A
5	D	15	A	25	D	35	D
6	D	16	A	26	A	36	B
7	C	17	A	27	A	37	D
8	C	18	D	28	C	38	B
9	D	19	D	29	A	39	B
10	D	20	C	30	B	40	D

CHAPTER-6

1	C	11	C	21	B	31	B	41	B
2	A	12	B	22	D	32	B	42	B
3	B	13	B	23	A	33	B	43	A
4	C	14	D	24	A	34	A	44	A
5	D	15	D	25	A	35	A	45	C
6	A	16	B	26	B	36	D	46	B
7	B	17	D	27	B	37	B	47	B
8	C	18	A	28	C	38	D	48	C
9	C	19	A	29	A	39	A	49	D
10	B	20	B	30	C	40	B	50	A

CHAPTER-7

1	D	11	B	21	D
2	A	12	D	22	A
3	D	13	A	23	A
4	B	14	B	24	A
5	D	15	D	25	C
6	A	16	D	26	B
7	C	17	D	27	C
8	A	18	A	28	B
9	C	19	B	29	A
10	A	20	A	30	D

CHAPTER-8

1	B	11	D	21	D	31	A
2	C	12	C	22	A	32	B
3	D	13	D	23	A	33	B
4	C	14	A	24	B	34	A
5	D	15	A	25	D	35	D
6	D	16	A	26	A	36	B
7	C	17	A	27	A	37	D
8	C	18	D	28	C	38	B
9	D	19	D	29	A	39	B
10	D	20	C	30	B	40	D

CHAPTER-9

1	A	11	A	21	B	31	C
2	B	12	B	22	B	32	A
3	D	13	C	23	C	33	B
4	B	14	C	24	D	34	B
5	D	15	C	25	B	35	A
6	C	16	C	26	B		
7	B	17	A	27	A		
8	B	18	A	28	C		
9	B	19	D	29	D		
10	D	20	B	30	C		

CHAPTER-10

1	C	11	A	21	C	31	A	41	C
2	B	12	D	22	D	32	A	42	D
3	B	13	B	23	B	33	D	43	B
4	D	14	B	24	B	34	A	44	C
5	B	15	A	25	A	35	A	45	B
6	B	16	A	26	A	36	D	46	B
7	C	17	A	27	A	37	A		
8	A	18	B	28	B	38	B		
9	C	19	B	29	D	39	B		
10	C	20	C	30	D	40	D		

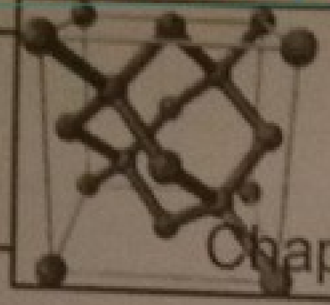
CHAPTER-11

1	B	11	D	21	D	31	A
2	D	12	A	22	A	32	B
3	C	13	C	23	B	33	A
4	C	14	A	24	B	34	B
5	B	15	B	25	B	35	B
6	B	16	B	26	D	36	D
7	A	17	A	27	A	37	A
8	C	18	B	28	D	38	C
9	C	19	B	29	B	39	D
10	A	20	A	30	A	40	C

KIPS ENTRY TEST SERIES

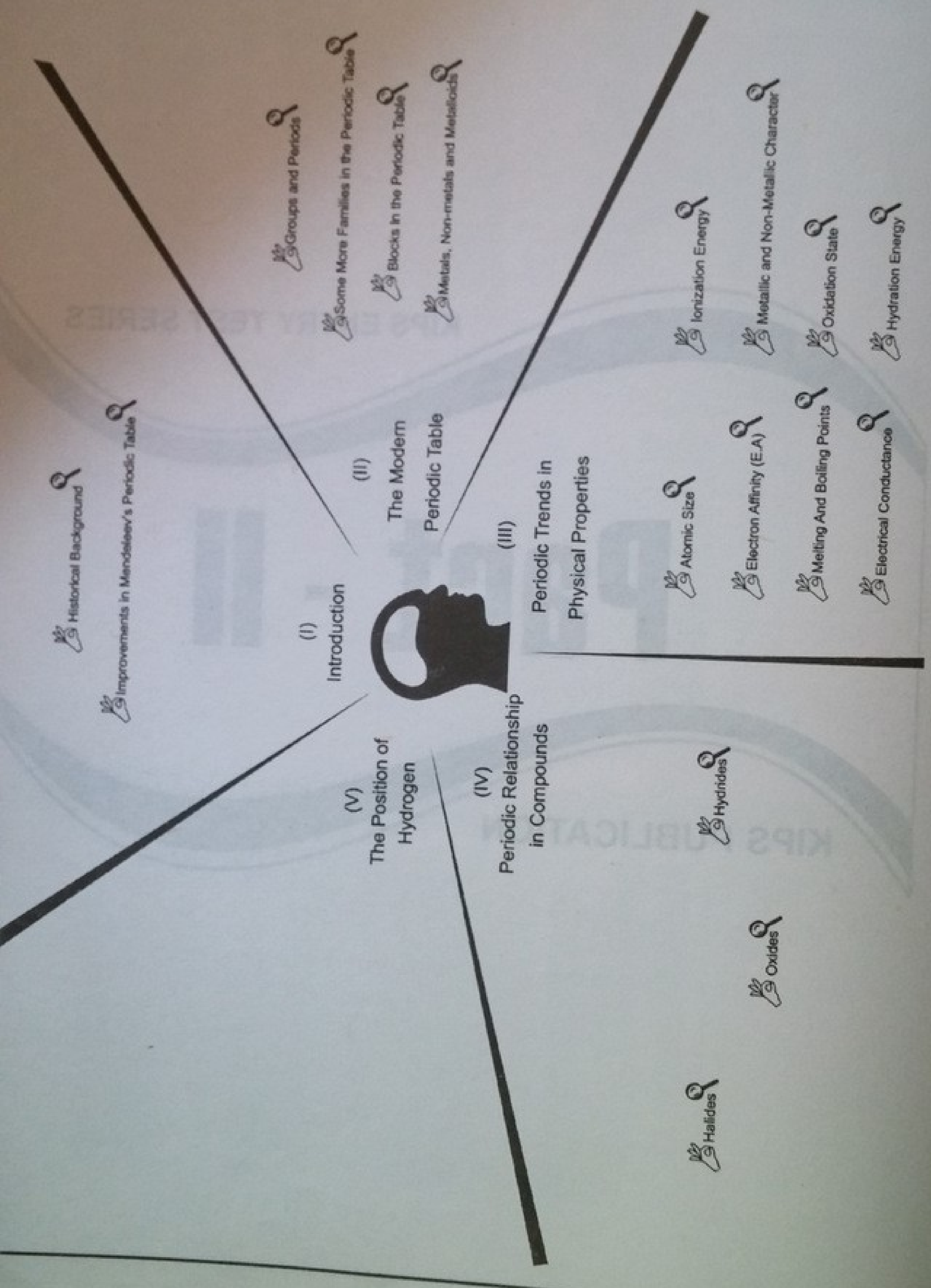
Part - II

KIPS PUBLICATION



Chapter 1

PERIODIC CLASSIFICATION OF ELEMENTS AND PERIODICITY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Improvements in Mendeleev's Periodic Table
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Chapter 1

Periodic Classification Of Elements & Periodicity

PURPOSE OF PERIODIC TABLE

The periodic table provides a basic framework to study the periodic behaviour of physical and chemical properties of elements as well as their compounds.

HISTORICAL BACKGROUND

Name of Scientist	Country	Contributions	Basis of Classification
Al-Razi	Arab	First ever classification	Physical and chemical properties of substances
Dobereiner	German	Law of triads	Elements can be classified in triads where the atomic weight of middle element of each triad is almost equal to the arithmetic mean of atomic weights of the other two elements.
Newland	English	Law of octaves	If elements are arranged in increasing order of their atomic weights, every 8th element starting from a given one has similar properties as that of first one. It includes 62 elements.
Mendeleev	Russian	Periodic law	The physical and chemical properties of elements are periodic functions of their atomic weights. His periodic table contains 12 periods and 8 groups.
Moseley	English	Modern periodic law	The physical and chemical properties of elements are periodic functions of their atomic numbers. It contains seven periods & eight groups.

Advantages of Mendeleev's Periodic Table

- Mendeleev left many vacant spaces in his periodic table for unknown elements and predicted their properties e.g. germanium.
- Mendeleev's Periodic Table helped to correct the doubtful atomic weights of elements e.g. beryllium.

Improvements in Mendeleev's Periodic Table

- Arrangement of elements in ascending order of atomic numbers to rectify four misfit pairs of elements in the Mendeleev's Periodic Table i.e. Ar & K, Co & Ni, Te & I and Th & Pa.
- Addition of group VIII to place the newly discovered noble gases properly.
- Introduction of two types of vertical groups A and B to eradicate the misplacement of Zn, Cd & Hg and Be, Mg, Ca, Sr & Ba in same vertical group and so many others in same manner.

MODERN PERIODIC TABLE

Modern periodic law (Moseley)

The physical and chemical properties of elements are the periodic function of their atomic numbers.

Chapter 1

Periodic Classification Of Elements & Periodicity

Modern Periodic Table

Periodic Table	Elements arranged in order of increasing proton number
Group Number	Number of electrons in outermost shell (valence electrons)
Period Number	Number of shells of electrons
Valence Electron	Electron in outermost shell
Metals	Elements with 1-3 valence electrons except boron
Non-metals	Elements with 4-7 valence electrons.
Inert gases	Elements with full outermost-shell

Essential Features

Following are the essential features of the modern periodic table:-

Groups

- The vertical columns of elements in the periodic table are called groups. Each group represents number of valence electrons.
- All the elements in a group have similar properties and similar electronic configuration of valence shell.
- There are eight groups that are shown by Roman numerals I to VIII.
- Each group has two sub-groups A and B. 'A' contains normal or typical elements while 'B' contains transition elements.

Periods

- The horizontal rows of elements in the periodic table are called periods.
- All elements in a period have same number of shells according to the period number.
- There are seven periods in the periodic table that are known by Arab numerals 1 to 7.

Sr#.	Peculiarity	Sub-groups present	No. of elements	s-block elements	p-block elements	d-block elements	f-block elements
1	Shortest	A	2	2	0	0	0
2	Short	A	8	2	6	0	0
3	Short	A	8	2	6	0	0
4	Long	A & B	18	2	6	10	0
5	Long	A & B	18	2	6	10	0
6	Longest	A & B	32	2	6	10	14
7	Incomplete	A & B	26	2	-	10	14

Families

Name	Contents
Alkali metals	Group-I A
Alkaline earth metals	Group II A
Chalcogens	Group-VI A
Halogens	Group VII A
Noble gases/Inert gases	Group VIII A
Coinage metals	Group I B
Rare earth elements / Inner transition metals	f-block elements
Actinides	fourteen elements that follow Actinium ($_{89}$Ac)
Lanthanides	fourteen elements that follow lanthanum ($_{57}$La)
Outer transition metals	d-block elements

Blocks

There are four blocks on basis of the sub-shell of the valence shell of element.

Block	Contents
s	IA & IIA & He
p	IIIA to VIIIA except He
d	Transition elements (outer) 3d-series, 4d-series and 5d-series
f	Actinides & Lanthanides 4f-series and 5f-series

Lanthanide Contraction

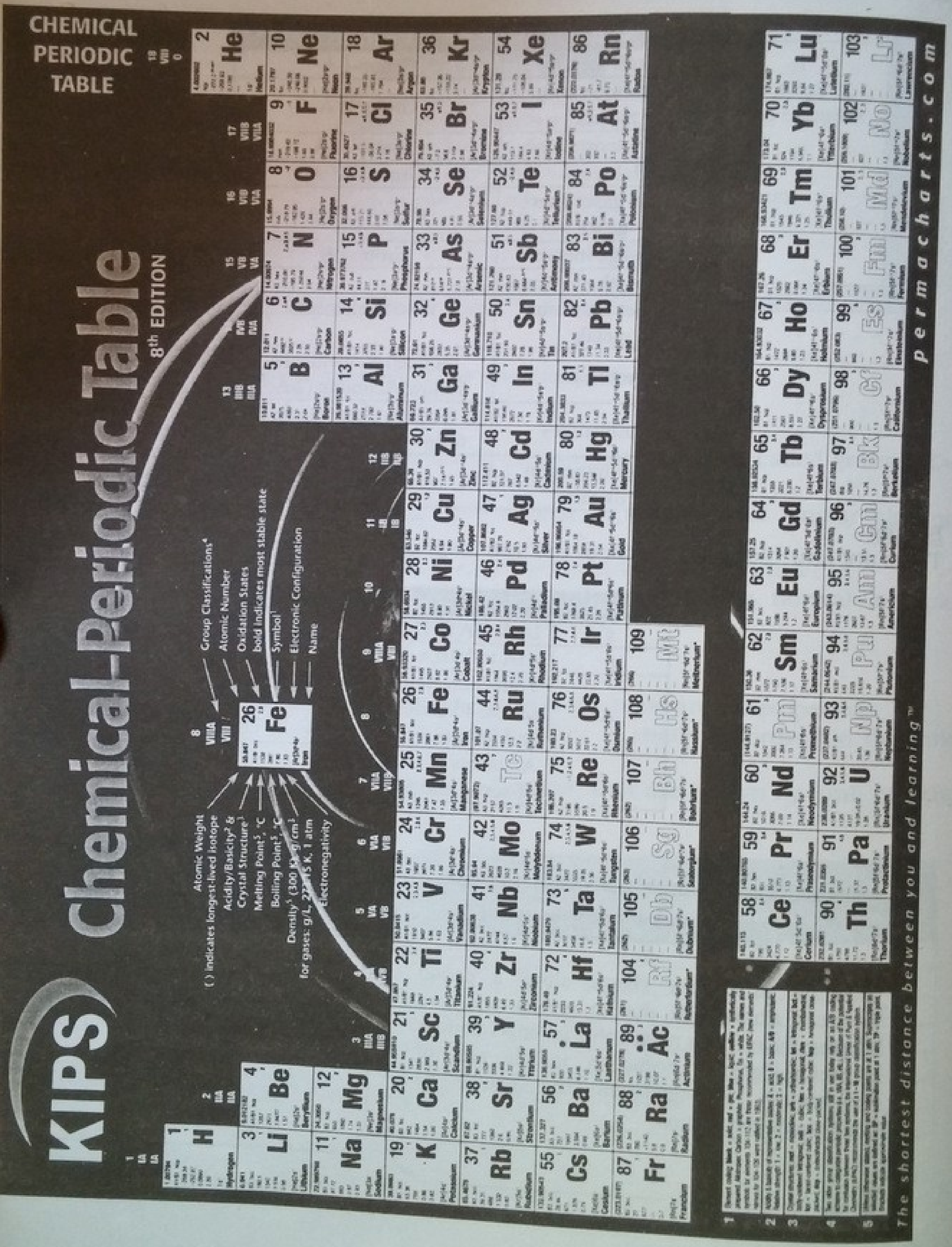
Increase in nuclear charge along a period reduces atomic size due to greater attractive forces; the effect is remarkable in longer periods therefore gradual reduction in the size of lanthanides is significant and known as lanthanide contraction.

+ve ion is always smaller than the neutral atom, whereas –ve ion is always larger than the neutral atom.

$$M^+ < M$$
$$X^- > X$$

Chapter 1

Periodic Classification Of Elements & Periodicity



KIPS Chemical Periodic Table

8th EDITION

CHEMICAL PERIODIC TABLE

Atomic Weight
( ) indicates longest-lived isotope
Acidity/Basicity² & Crystal Structure³
Melting Point⁵, °C
Boiling Point⁵, °C
Density⁵ (300 K) g/cm³
for gases: g/L, 273.15 K, 1 atm
Electronegativity
Group Classifications⁴
Atomic Number
Oxidation States
bold indicates most stable state
Symbol¹
Electronic Configuration
Name

26 Fe Iron

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt									

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

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Chapter 1

Periodic Classification Of Elements & Periodicity

METALS, NON-METALS AND METALLOIDS

Metals	Non-metals	Metalloids
• Usually solids at room temperate (except Hg) • High melting and boiling points (except Group I) • Good conductors of heat and electricity • Often shiny, ductile, malleable and possess great tensile strength • Mostlly form ionic compound • Oxides are usually basic or amphoteric • Often form hydrogen gas with dilute acids • Always form positive ions (cations)	• Often gases (except $Br_{(l)}$, $S_{(s)}$, P(s), I(s), C(s), B(s) and Si(s) • Low melting and boiling points (except B, C and Si) • Poor conductor of heat and electricity (except Graphite) • Normally dull, soft and cannot be drawn out into wires or made into flat sheets. • Most compounds are covalent • Oxides are usually neutral or acidic • Always form negative ions (anions)	• Their electron losing and gaining capabilities are intermediate between metals and non metals. • Their electrical and thermal conductivities are intermediate between metals and non metals. • Their oxides are amphoteric, which means that they can act as acidic and basic oxides.

POSITION OF HYDROGEN IN PERIODIC TABLE

Hydrogen resembles with elements of groups IA, IVA and VIIA. Its actual position is still confusing because of its behaviour.

Position over Alkali Metals (I-A)

Similarities	Differences
• One electron in outermost shell • Ability to lose electron and form positive ions • Strong tendency to combine with electronegative elements like halogens. • Formation of H^+ on ionization of its ionic compounds • Collection at cathode during electrolysis	• It is a gas where as I-A elements are solid metals. • It needs only one electron to complete its outer most shell others need seven. • It prefers to form covalent compounds. • It exists in diatomic state. • It can form H^- ion. • Its oxide is neutral e.g. H_2O.

Position Over Halogens (Group-VII-A)

Similarities	Differences
• Gaseous state • Stable diatomic molecules Requirement of only one electron to complete their valence shell • Formation of hydrides similar to alkali metal halides Formation of hydride ion H^- like F^-, Cl^-, I^- etc.	• It has only one valence electron while halogens have seven. • H^- ion is unstable in aqueous solution but halide are stable. • It can form H^+ ion. • It is liberated at cathode during electrolysis but halides at anode. • Its oxide is neutral but the oxides of halogens are acidic.

Position over Carbon-Silicon Family (Group-IVA)

Similarities	Differences
• Half-filled valence shell • Mutual sharing of electrons during chemical interactions • Remarkable reducing property	• It is a gas. • It needs only one electron to complete its valence shell. • It exists as diatomic molecules.

PERIODIC TRENDS IN PHYSICAL PROPERTEIS

Property	Definition	Trend in a group (down the group)	Responsible Factors.	Trend along a period (from left to right)
Atomic radius	Half of the distance between the centers of two adjacent atoms of any element.	Increases	Nuclear charge and no. of shells	Decreases
Ionic radius	Distance between the center of an ion and the outer boundary of its electron cloud.	(for similar charged ions)increases	Nuclear charge and no. of shells.	Decreases for iso-electronic +ve and –ve ions.
Ionization energy	Minimum quantity of energy, which is required to remove an electron from the outer most shell of its isolated, gaseous atom in its ground state.	Decreases	Nuclear charge, atomic size and shielding effect.	Increases
Electron affinity	Energy released or absorbed, when an electron is added to a gaseous atom to form a negative ion.	Decreases	Size of atom, nuclear charge and vacancies in valence shell.	Increases
Metallic character	Tendency to lose electron & form cations and basic oxides.	Increases	Atomic size and nuclear charge.	Decreases
Melting & boiling points	Specific temperature at which an element changes to liquid or gaseous state.	for IA and IIA decreases. for VIIA increases	No. of valence electrons.	I-A to IV-A increases V to VIII decreases
Oxidation state	Charge, which an element could carry in a compound.	Usually same	Electrons lost or gained	I to IV same as group number V,VI,VII is equal to vacancy or group number
Electrical conductance	Ability to conduct electricity.	(increases for IA & IIA) no regular trend for transition metals	Lose electrons in outer shell	Decreases
Hydration energy	Heat absorbed or evolved, when one mole of gaseous ion dissolves in water to give an infinitely dilute solution.	Decreases	Charge to size ratio	Increases

PERIODIC RELATIONSHIP IN COMPOUNDS

Halides

The binary compounds of halogens with other elements are called halides.

- There are three classes of halides: ionic, covalent & polymeric.

Characteristics	Ionic	Covalent	Polymeric
Intramolecular forces	Purely ionic	Covalent	Partly ionic
Elements (Other than halogen) involved	Strongly electropositive	Less electropositive	Less electropositive
Lattice structure	Crystalline solid	Gases or liquids	Layer or chain form
Basic unit	Discrete ions	Discrete molecules	Discrete molecules
Melting & boiling point	High	Low	Moderate
Examples	NaCl, $CaCl_2$	CCl_4	$AlCl_3$, $BeCl_2$ & $SiCl_4$

- If an element forms more than one halides, the halide in its lower oxidation state tends to be ionic e.g. $PbCl_2$ is mainly ionic and $PbCl_4$ is fairly covalent due to high polarizing power.
- Order of decreasing ionic character of halides:

  fluoride > chloride > bromide > iodide
- Bonding Character of Chlorides of Third Period

Groups	I A	II A	III A	IV A	V A	VI A
Chlorides	NaCl	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	S_2Cl_2
Character	Ionic	Partly ionic	Partly ionic	Polar covalent	Polar covalent	Polar covalent

Hydrides

The binary compounds of hydrogen with other elements are called hydrides.

- There are three classes of hydrides: ionic, covalent & intermediate.

Characteristics	Ionic	Covalent	Intermediate
Intramolecular forces	Purely ionic	Covalent	Partly ionic
Elements (other than hydrogen) involved	Strongly electropositive	Less electropositive	Less electropositive
Structure	Crystalline solid	Gases or volatile liquids	Polymeric (layer or chain form)
Basic unit	Discrete ions	Discrete molecules	Discrete molecules
Melting point & Boiling point	High	Low	-
Electrical conductance	Conductors in molten state	Non-conductors	-
Examples	NaH, CaH_2	H_2O, H_2S &PH_3	BeH_2 & MgH_2

- Boiling point of water is greater than HF although it is less polar

xides

he binary compounds of oxygen are called oxides

lassification of Oxides

xides can be classified on the basis of

(i) Nature of chemical bonding
(ii) Acidic, basic or neutral

lassification on the basis of Acidic properties

(i) Basic oxides (Na_2O, K_2O, MgO, CaO etc)
(ii) Acidic oxides (CO_2, SO_3, SiO_2, NO_2 etc)
(iii) Amphoteric oxides (ZnO, Al_2O_3, BeO, Ga_2O_3, In_2O_3, GeO_2, SnO_2, PbO, As_2O_3, Sb_2O_3, Bi_2O_3,

AXIMAS AND MINIMAS OF PERIODIC TABLE

Largest block of periodic table	⇒d-block (40 elements)
Longest period of periodic table	⇒6th period (32 elements)
Largest group of periodic table	⇒VIII-B (12 elements)
Most metallic element	⇒Cesium
Most powerful reducing agent	⇒Cesium
Most reactive metal	⇒Cesium
Most powerful oxidizing agent	⇒Fluorine
Least metallic element	⇒Fluorine
Most reactive non-metal	⇒Fluorine
Element having highest ionization energy	⇒Helium
Element having highest electron affinity value	⇒Chlorine
Lowest value of oxidation state	⇒0 for an element in free state
Highest value of oxidation state (metal)	⇒Os^{+8}
Elements with no vacancy in valence shell	⇒Noble gases (0-group)
Elements with highest electrical conductance values	⇒I-B (coinage metals)
Halides having highest lattice energies	⇒Fluorides
Halides with strongest Vander Waals forces	⇒Iodides
Element forming most stable hydrides	⇒Fluorine
Elements forming least stable hydrides	⇒Thallium, Lead, Bismuth

PRACTICE EXERCISE

1. Elements in the same vertical group of the periodic table have same:
(a) Number of valence electrons
(b) Atomic number
(c) Atomic mass
(d) Atomic volume

2. An element having low value of ionization energy and low value of e
affinity is likely to belong to
(a) Group IA
(b) Group IIA
(c) Group VIIA
(d) Group VIII

3. Which set of elements is listed in order of increasing ionization energy?
(a) Sb<As<S<P<Cl
(b) Cl<Sb<P<As<S
(c) As<Cl<P<S<Sb
(d) Sb<As<Cl<S<P

4. Which of the following always increases on going from top to bottom in a
(a) Metallic character
(b) Electronegativity
(c) Oxidizing power
(d) Tendency to get reduced

5. Which of the p-block elements are not representative elements?
(a) Alkali metals (I-A)
(b) Group-14 elements (IV-A)
(c) Group-18 elements (VIII-A)
(d) Halogens (VII-A)

6. Among halogens, the highest boiling point is of
(a) Fluorine
(b) Chlorine
(c) Bromine
(d) Iodine

7. Which of the following will not form crystalline structure with opp
charged ions
(a) H^+
(b) H^-
(c) Mg^{2+}
(d) Ca^{2+}

8. Which statement is incorrect?
(a) All the metals are good conductor of electricity.
(b) All the metals are good conductor of heat.
(c) All the metals form positive ions.
(d) All the metals form acidic oxides.

9. Periodic table provides a basic framework to study elements with resp
their
(a) Physical properties
(b) Chemical properties
(c) Properties of their compounds
(d) All

10. The scientist who did not contribute in the construction of periodic table?
(a) Al-Razi
(b) Moseley
(c) Dobereiner
(d) Democritus

11. Concept of Triads was introduced by
(a) Dobereiner
(b) Newlands
(c) Mendeleev
(d) Al-Razi

12. Which element was not known when Mendeleev proposed his classification
(a) Hydrogen
(b) Sodium
(c) Copper
(d) Germanium

13. Elements with similar chemical properties appear in the
(a) Same family
(b) Same period
(c) p block elements
(d) Right upper corner

PRACTICE EXERCISE

35 mins
Time Yourself

1. Elements in the same vertical group of the periodic table have same.
   (a) Number of valence electrons
   (b) Atomic number
   (c) Atomic mass
   (d) Atomic volume
2. An element having low value of ionization energy and low value of electron affinity is likely to belong to
   (a) Group IA
   (b) Group IB
   (c) Group VIIA
   (d) Group VIII
3. Which set of elements is listed in order of increasing ionization energy?
   (a) $Sb<As<S<P<Cl$
   (b) $Cl<Sb<P<As<S$
   (c) $As<Cl<P<S<Sb$
   (d) $Sb<As<Cl<S<P$
4. Which of the following always increases on going from top to bottom in a group?
   (a) Metallic character
   (b) Electronegativity
   (c) Oxidizing power
   (d) Tendency to get reduced
5. Which of the p-block elements are not representative elements?
   (a) Alkali metals (I-A)
   (b) Group-14 elements (IV-A)
   (c) Group-18 elements (VIII-A)
   (d) Halogens (VII-A)
6. Among halogens, the highest boiling point is of
   (a) Fluorine
   (b) Chlorine
   (c) Bromine
   (d) Iodine
7. Which of the following will not form crystalline structure with oppositely charged ions
   (a) H^+
   (b) H^-
   (c) Mg^{2+}
   (d) Ca^{2+}
8. Which statement is incorrect?
   (a) All the metals are good conductor of electricity.
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   (c) Properties of their compounds
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    (a) Hydrogen
    (b) Sodium
    (c) Copper
    (d) Germanium
13. Elements with similar chemical properties appear in the
    (a) Same family
    (b) Same period
    (c) p block elements
    (d) Right upper corner

Noble gases are named so because they are
(a) less reactive (b) Zero group elements
(c) Having completely filled valence shell (d) All.

In modern periodic table, all the elements are arranged in ascending order of
(a) Valency (b) Atomic mass
(c) Atomic number (d) Valence electrons

The longest period in the modern periodic table is
(a) 6th (b) 7th
(c) 2nd & 3rd both (d) 5th

Inner transition elements are called
(a) Lanthanides (b) Actinides
(c) Rare earth metals (d) All

Seventh period contains __________ normal elements.
(a) 2 (b) 4
(c) 6 (d) 8

Modern periodic table has been divided in __________ blocks.
(a) 2 (b) 4
(c) 8 (d) 7

Non-metals usually form __________ oxides.
(a) Acidic (b) Amphoteric
(c) Neutral (d) All of the above

Amphoteric oxides are those, which possess __________ properties.
(a) Acidic (b) Basic
(c) Acidic and basic (d) Neutral and acidic

Best position of hydrogen in the periodic table is above I.A Group which is mainly due to
(a) Both are electropositive
(b) Similar outer most shell electronic configuration
(c) Both form ionic compounds
(d) All

Hydrogen resembles with carbon because of having
(a) Same number of electrons in the valence shell
(b) Similar physical state
(c) Remarkable reducing properties
(d) Homovalent (show same valency)

Which one of the following sets consists of all coinage metals?
(a) Cu, Hg, Au (b) Cu, Ag, Au
(c) Ag, Au, Hg (d) Cu, Fe, Au

In which of the following pairs are elements belonging to the same group?
(a) Boron & Beryllium (b) Nitrogen & Phosphorous
(c) Magnesium & Aluminium (d) Gallium & Helium

Many properties of an element and its compounds can be predicted from the position of the element in the periodic table. What property could not be predicted in this way?
(a) The nature of its oxides (b) The charge on its ions
(c) The formula of its oxide (d) Its number of isotopes

Which one of the following is not a periodic property?
(a) Melting point of elements (b) Boiling point of elements
(c) Ionization energy of elements (d) Coordination number of ions

The atomic radii decreases by increasing atomic number in
(a) Alkali metal (b) Alkaline earth metal
(c) Elements from Li to Ne (d) Halogens

29. Which discovery caused a revision in the periodic law as stated by Mendeleev?
(a) Location of nucleus by Rutherford
(b) Atomic number by Moseley
(c) X-rays by Roentgen
(d) Natural radioactivity by Henry Bacquerel.

30. An element has electronic configuration $1s^2, 2s^2, 2p^2$. It belongs to
(a) Group II-A
(b) Group IV-A
(c) Group VII-A
(d) Group VI-A

31. The property which increases upto group IV-A then decreases onwards
(a) Ionization energy
(b) Atomic radii
(c) Melting & boiling points
(d) Atomic volume

32. Which of the following ion is stable in aqueous solution?
(a) H^+
(b) H^-
(c) Cl^-
(d) All are stable

33. The atoms of same element having same atomic number but different mass number are called
(a) Isobars
(b) Isomers
(c) Isotopes
(d) Isotropes

34. Deuterium reacts with oxygen to form
(a) Hard water
(b) Heavy water
(c) Soft water
(d) Water gas

35. Which order of ionization energy is correct.
(a) Mg < Al
(b) Si > P
(c) Mg > Al
(d) both b & c

36. Ionization energy depends upon
(a) Nuclear charge
(b) Atomic size
(c) Shielding effect
(d) I.E depends upon all of the above and nature of orbital

37. Shielding effect across the period
(a) Increases
(b) Decreases
(c) Can not be predicted
(d) Remains constant

38. Addition of 2nd electron to a uninegative ion is always
(a) Exothermic
(b) Endothermic
(c) Data is insufficient
(d) Unpredictable

39. Higher value of electron affinity means
(a) Atom will lose electron easily
(b) Atom will gain electron easily
(c) Atom may form di-positive ion
(d) The reason is unknown

40. Metallic characters of alkali metals
(a) Increase down the group
(b) Decrease down the group
(c) No regular trend
(d) Remain same.

41. Melting points of VII-A group elements down the group
(a) Increase
(b) Decrease
(c) Remain constant
(d) No regular trend

42. Oxidation state of an atom represents
(a) Number of electrons gained
(b) Number of electrons lost
(c) Apparent charge in compound.
(d) Its vacancies

43. Which of the following possesses maximum hydration energy?
(a) Na^+
(b) K^+
(c) Mg^{+2}
(d) Ca^{+2}

44. Halides in which halogen atoms act as a bridge between two atoms of the other element are called
(a) Covalent halides
(b) Electronegative halides
(c) Polymeric halides
(d) Polymeric hydrides

5. Less electronegative elements such as Be, Ga, Aℓ etc form
(a) Polymeric halide (b) Covalent halide
(c) Ionic halide (d) All

6. Iodine is solid due to
(a) Strong covalent bond (b) Large value of dipole moment
(c) High polarizability (d) Strong hydrogen bonding

47. True increasing order of acidity of the oxides of Mn is
(a) $MnO < MnO_2 < Mn_2O_7$ (b) $Mn_2O_7 > MnO_2 > MnO$
(c) $MnO_2 > MnO > Mn_2O_7$ (d) $MnO_2 > Mn_2O_7 > MnO$

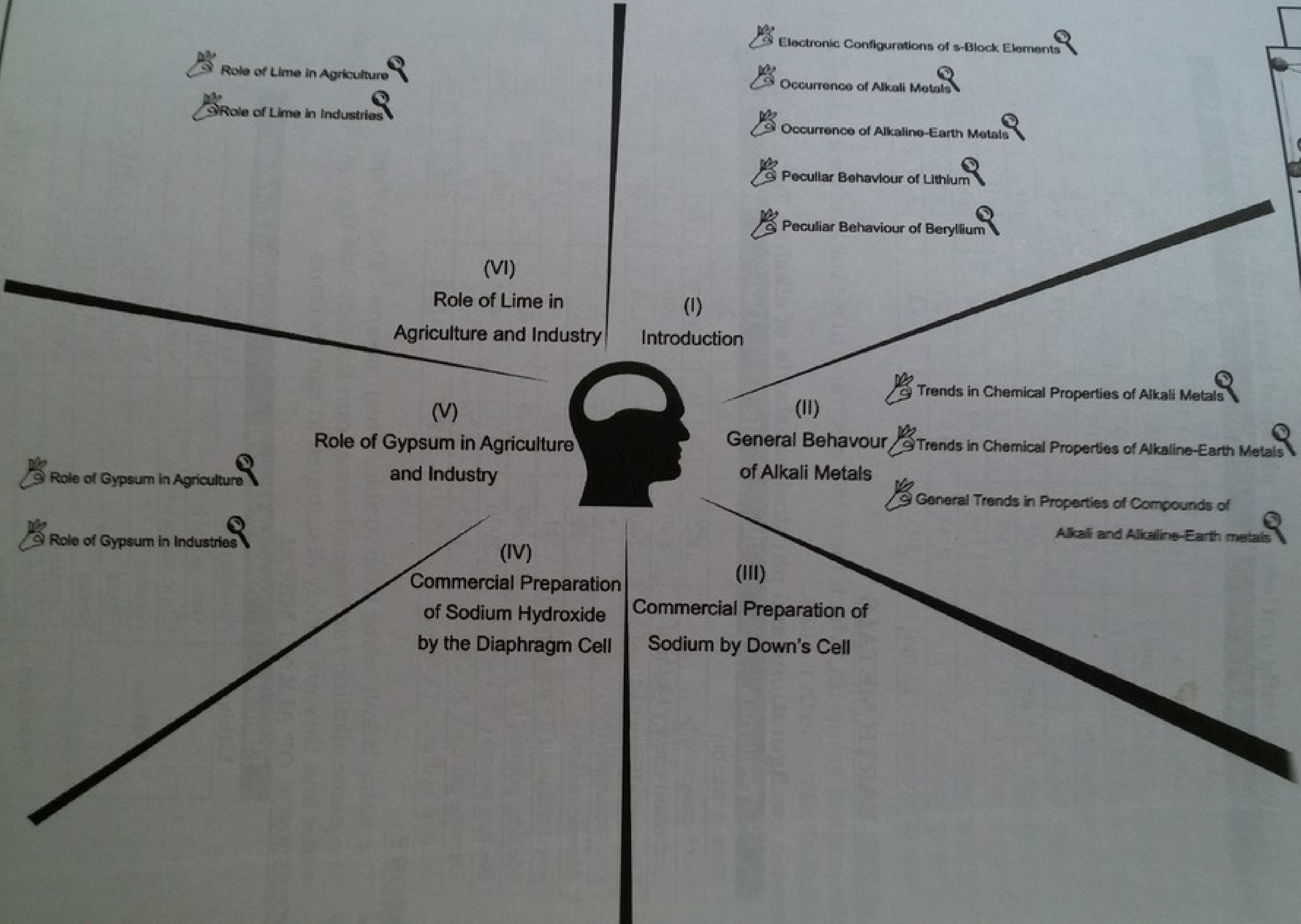
48. Keeping in view the size of atom which order is correct one?
(a) Mg > Sr (b) Ba > Mg
(c) Lu > Ce (d) Cl > I

49. Which one of the following element has highest oxidation state in its compounds?
(a) Cr (b) Mn
(c) Sn (d) O

50. Which of the following cannot exist in solution
(a) O^{-2} (b) H^+
(c) Cl^- (d) Na^+

Chapter 2

s–BLOCK ELEMEN



(I)
Introduction

- Electronic Configurations of s-Block Elements
- Occurrence of Alkali Metals
- Occurrence of Alkaline-Earth Metals
- Peculiar Behaviour of Lithium
- Peculiar Behaviour of Beryllium

(II)
General Behaviour of Alkali Metals

- Trends in Chemical Properties of Alkali Metals
- Trends in Chemical Properties of Alkaline-Earth Metals
- General Trends in Properties of Compounds of Alkali and Alkaline-Earth metals

(III)
Commercial Preparation of Sodium by Down's Cell

(IV)
Commercial Preparation of Sodium Hydroxide by the Diaphragm Cell

(V)
Role of Gypsum in Agriculture and Industry

- Role of Gypsum in Agriculture
- Role of Gypsum in Industries

(VI)
Role of Lime in Agriculture and Industry

- Role of Lime in Agriculture
- Role of Lime in Industries

ALKALI METALS

he elements of group IA except hydrogen, which have only one electron in s-orbital of heir valence shell, are called alkali metals.

Electronic Configurations and physical constants of Alkali Metals

Properties	Li	Na	K	Rb	Cs
Atomic number	3	11	19	37	55
Electronic configuration	$1s^2 2s^1$	[Ne] $3s^1$	[Ar] $4s^1$	[Kr] $5s^1$	[Xe]6s
Ionization energy (kJ/mol)	520	496	419	403	376
Electron affinity (kJ/mol)	-60	-53	-48	-47	-46
Electronegativity	1.0	0.9	0.8	0.8	0.7
Atomic radius	123	158	203	216	235
Ionic radius of 1+ ion (ppm)	60	95	133	148	169
Melting points (^{0}C)	187	97.5	63.6	39.0	28.5
Boiling points (^{0}C)	1325	889	774	688	690
Density gm/cm^3(20^{0}C)	0.53	0.97	0.86	1.53	1.9
Heat of hydration (kJ/mol)	505	475	384	345	310

ALKALINE-EARTH METALS

The elements of group IIA, which have two electrons in s-orbital of their valence shell, are called alkaline earth metals.

Electronic configurations and physical constants of alkaline Earth Metals

Properties	Be	Mg	Ca	Sr	Ba
Atomic number	4	12	20	38	56
Electronegativity	$1s^2 2s^2$	[Ne] $3s^2$	[Ar] $4s^2$	[Kr] $5s^2$	[Xe]$6s^2$
Ionization energy (kJ/mol)	899	738	590	549	503
Electron affinity (kJ/mol)	240	230	156	168	52
Electronegativity	1.5	1.2	1.0	1.0	1.0
Atomic radius	89	136	174	191	198
Ionic radius of 2+ ion (ppm)	31	65	99	113	135
Melting points (^{0}C)	1289	649	839	769	725
Boiling points (^{0}C)	2970	1107	1484	1384	1640
Density gm/cm^3(20^{0}C)	1.85	1.74	1.55	2.6	3.5
Heat of hydration (kJ/mol)	2337	1897	1619	1455	1250

HISTORY

- The name 'alkali' came from Arabic, which means " The Ashes".
- The name alkaline earth metal came from the fact that they produce alkalies in water and they are widely distributed in earth's crust.

OCCURRENCE OF ALKALI METAL

Element	Name of Mineral	Chemical Formula
Lithium	Spodumene	$LiAl(SiO_3)_2$
Sodium	Rock salt (Halite)	NaCl
	Chile saltpeter	$NaNO_3$
	Natron	$Na_2CO_3.H_2O$
	Trona	$Na_2CO_3.2NaHCO_3.2H_2O$
	Borax	$Na_2B_4O_7.10H_2O$
Potassium	Carnallite	$KCl.MgCl_2.6H_2O$
	Sylvite	KCl
	Alunite	$K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$

OCCURRENCE OF ALKALINE EARTH METALS

Element	Name of Mineral	Chemical Formula
Beryllium	Beryl	$Be_3Al_2(SiO_3)_6$
	Chrysoberyl	Al_2BeO_4
Magnesium	Magnesite	$MgCO_3$
	Dolomite	$MgCO_3.CaCO_3$
	Carnallite	$KCl.MgCl_2.6H_2O$
	Epsom salt	$MgSO_4.7H_2O$
	Soap stone(talc)	$H_2Mg_3.(SiO_3)_4$
	Asbestos	$CaMg_3(SiO_3)_4$
Calcium	Calcite (Lime stone)	$CaCO_3$
	Gypsum	$CaSO_4.2H_2O$
	Plaster of Paris	$CaSO_4.1/2H_2O$
	Fluorite	CaF_2
	Phosphorite	$Ca_3(PO_4)_2$
Strontium	Strontionite	$SrCO_3$
Barium	Barite (Heavy Spar)	$BaSO_4$

PECULIAR BEHAVIOUR OF LITHIUM AND BERYLLIUM

Li (1st Alkali Metal)	Other Alkali Metals
Li is much harder and lighter than other I-A group	Other elements are soft
Li salts are insoluble in water	Salts of other elements are soluble
Forms stable complex compounds	Do not form complex compounds
Reacts slowly with water	React very fast with water
Does not form bi-carbonate, tri-iodide or hydrogen sulphide due to high polarizing power	Forms bi-carbonates, tri-iodide and hydrogen sulphide
Gives normal oxides on burning	Give peroxide and superoxide
Hydrides are very stable	Hydrides are less stable
Compounds are more covalent and soluble in organic solvent	Compounds are ionic and insoluble in organic solvent
Least reactive among IA group	Very reactive
Li does not react with acetylene	React with acetylene
Less electropositive	More electropositive
Carbonates and nitrates are unstable	Carbonates and nitrates are stable
LiOH on heating gives Li_2O	Hydroxide are stable
Gives nitride on reaction with N_2	No reaction with nitrogen
Gives carbide directly	No reaction with carbon directly

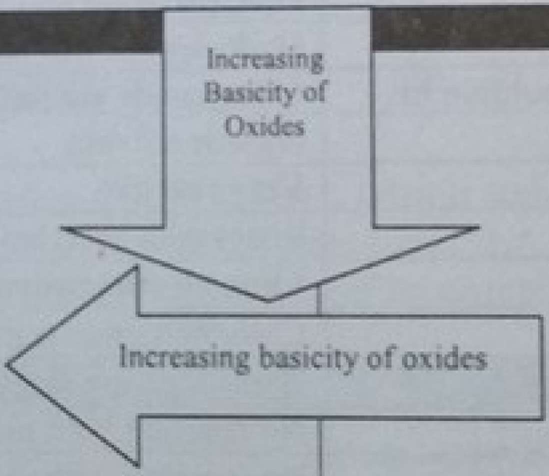
Be (1st Member of II-A)	Other members of II-A
Harder as Fe	Softr but harder than I-A group
M.P and B.P are higher	Less M.P and B.P than Be
Forms insoluble BeO with water	Form soluble oxide with water
Have resistance to complete oxidation	Oxidized completely
Liberates H_2 on reaction with alkalies	No reaction

TREND IN CHEMICAL PROPERTIES OF ALKALI & ALKALINE METALS

	Alkali Metals	Alkaline Metals
Valency	Low I.P & forms +1	Low I.P & form +2 ion
2nd I.P.	2nd I.P is very high	2nd I.P is comparatively low
Oxides	Normal, superoxide and peroxides are formed e.g. $Li + O_2 \rightarrow Li_2O$ (Normal Oxide) $Na + O_2 \rightarrow Na_2O_2$(Normal peroxide) $K + O_2 \rightarrow KO_2$ (Super oxide)	Normal and peroxides are produced e.g. $2Be + O_2 \rightarrow 2BeO$(Normal Oxide) $2Mg + O_2 \rightarrow 2MgO$(Normal Oxide) $2Ba + O_2 \rightarrow BaO_2$(Per oxide)
Hydrides	Ionic hydrides formation $2M + H_2 \rightarrow 2MH$	Ionic Hydride formation in presence of catalyst(MgI_2) $Mg + H_2 \rightarrow MgH_2$
Nitrides	Only Li give nitride directly	All elements give nitride directly
Sulphides	Form sulphides with S (M_2S)	Forms sulphides with S (MS)
Reaction with water	Reacts with water give MOH	React with water give $M(OH)_2$ except Be
Reaction with halogen	Reacts with halogen to give MX	React with halogen to give MX_2

- Reaction of alkali metal oxide with water is acid-base and not oxidation-reduction reaction. $O^{-2} + H_2O \rightarrow 2OH^-$

Group I – A	Group II – A
Lithium oxide (basic)	Beryllium oxide (basic)
Sodium oxide (basic)	Magnesium oxide (basic)
Potassium oxide (basic)	Calcium oxide (basic)



Chapter 2

s–Block Elements

TREND IN PROPERTIES OF COMPOUNDS OF ALKALI AND ALKALINE EARTH METALS

Alkali Metal	Alkaline Metals
OXIDES:	
Li - forms normal oxide, Na – forms per oxide, other form super oxides.	BeO is amphoteric others are basic in nature
All oxides are soluble and forms OH^- in water	Be and Mg do not react with water while other oxides soluble in water and form OH^-
KO_2 absorbs CO_2 and liberate O_2 used in breathing equipments.	
Solubility increases down the group	Solubility increases down the group
Aqueous solution is highly alkaline	Aqueous solution is less alkaline
HYDROXIDE:	
These are hygroscopic, very soluble in water except LiOH	$Be(OH)_2$ is insoluble, $Mg(OH)_2$ is sparingly soluble and $Ba(OH)_2$ is more soluble
Difficult to decompose	Decomposes on heating
	Milk of lime is used in test of CO_2
	Milk of Magnesia is used against acidity of stomach
CARBONATES:	
Carbonates are very soluble in water except $LiCO_3$	Carbonates are insoluble in water
Thermally stable except Lithium	Thermally less stable
Decomposition on heating decreases down the group	Decomposition on heating decreases down the group
NITRATES:	
Nitrates are soluble in water	Nitrates are soluble in water
Nitrates of Li gives Li_2O, O_2 and NO_2 on heating other form nitrite and oxygen $NaNO_3 \rightarrow NaNO_2 + O_2$	Nitrates of Mg, Ca, Ba give NO_2, O_2 and metallic oxide
SULPHATES:	
Sulphates are soluble in water except Lithium	Solubility decreases down the group

COMMERCIAL PREPARATION OF SODIUM

Melting point of NaCl is 801°C. It is reduced to 600°C by addition of $CaCl_2$ (flux).

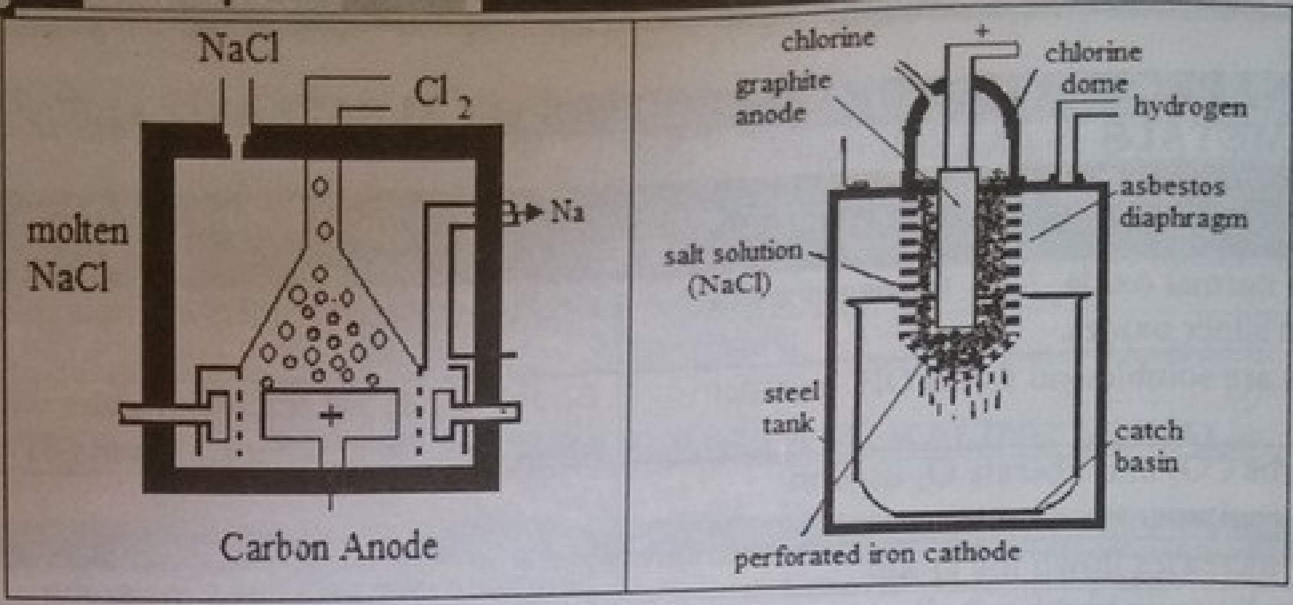
$$NaCl_{(fused)} \rightarrow Na_{(99.9\%\ pure)} + \frac{1}{2} Cl_2$$

Down's cell

- Anode is made up of graphite. (Cl_2 is collected)
- Cathode is of iron. (Na is collected)

Advantages of Down's cell

- The metallic fog is not produced
- Liquid sodium can easily be collected at 600°C
- Material of the cell is not attacked by the products formed during the electrolysis.



COMMERCIAL PREPARATION OF SODIUM HYDROXIDE

Sodium hydroxide (caustic soda) is manufactured on a large scale by the electrolysis of aqueous solution of common salt (Brine) in a diaphragm cell.

PREPARATION OF NaOH

Brine

30% aqueous solution of NaCl is called Brine.

- NaOH is prepared from brine.
- Cathode is made up of steel lined with asbestos..
- Anode is made up of graphite.
- Steam helps to keep perforation of cathode clear.
- H_2 is produced at cathode.
- Reaction between Cl_2 and OH^- is stopped by using asbestos diaphragm.
- OH^- may not contaminate Cl_2 on oxidation at anode for which anode level is slightly higher to keep liquid to flow towards cathode.
- Solution of NaOH obtained contains 11% NaOH and 16% NaCl.
- After evaporation, NaOH crystallizes and contains 50% NaOH and 1% NaCl as impurity.

ROLE OF GYPSUM IN AGRICULTURE

- $CaSO_4.2H_2O$ is gypsum.
- Applied to soil to provide Ca and S.
- Leached soils are supplied by gypsum.
- Sulphur develops protein and chlorophyll in plants.
- Due to deficiency of S, plants become pale green coloured.
- Root system of plants is enlarged by sulphur.

ROLE OF GYPSUM IN INDUSTRIES

- $CaSO_4.1/2H_2O$ is plaster of Paris.
- Plaster of Paris is used in making plaster walls, casts of statuary and coins in holding of fractured bones.
- In cement, plaster is added to prolong the time of setting.
- Hard finish plasters are achieved by the calcinations of anhydrous sulphates with alum or borax.

- Hard finish plasters are used in construction of buildings as wall boards and partitions.
- Gypsum is used in paper industry as filler.

ROLE OF LIME IN AGRICULTURE

- Lime neutralizes the acidic salts.
- Lime-sulphur spray is prepared from lime and has strong fungicidal affect.
- Slaking of lime is exothermic reaction & $Ca(OH)_2$ is formed.
- It increases the solubility of phosphorous in acidic soils.
- Calcium increases the size of root hair and root system.
- Calcium is essential for normal growth of leaf.
- Calcium is important for microorganism, which produces nitrate.
- Deficiency of calcium stimulates the accumulation of Al & Mn.

ROLE OF LIME IN INDUSTRY

Lime is used in:

- Extraction and refining of metal.
- Paper industry.
- Glass and ceramic industry.
- Preparation of mortar
- Mortar (contains slaked lime (one vol.), sand (3 or 4 vol.) and water.
- Refining of raw sugar.
- Leather industry
- Preparation of CaC_2
- As dehydrating agent in combination with NaOH forms soda lime.

GARDEN OF EQUATIONS

Reactions of Metals with Water

$$2Li + 2H_2O \longrightarrow 2LiOH + H_2$$
$$2K + 2H_2O \longrightarrow 2KOH + H_2$$

Reactions of Metallic Oxides with Water

$$Na_2O + 2H_2O \longrightarrow 2NaOH$$
$$2CaO + 2H_2O \longrightarrow 2Ca(OH)_2$$
$$Li_2O + H_2O \longrightarrow 2LiOH$$
$$2Na_2O_2 + 2H_2O \longrightarrow 4NaOH + O_2$$

Effect of Heat on Hydroxides

$$Ca(OH)_2 \xrightarrow{\Delta} CaO + H_2O$$
$$2LiOH \xrightarrow{\Delta} Li_2O + H_2O$$

Reactions of Metals with Oxygen

$$4Li + O_2 \longrightarrow 2Li_2O$$
$$2Na + O_2 \xrightarrow{\Delta} Na_2O_2$$

Effect of Heat on Carbonates

$$Li_2CO_3 \longrightarrow Li_2O + CO_2$$
$$CaCO_3 \longrightarrow CaO + CO_2$$

Formation of Bicarbonates from Carbonates

$$Na_2CO_3 + H_2O + CO_2 \xrightarrow{\Delta} 2NaHCO_3$$
$$CaCO_3 + H_2O + CO_2 \xrightarrow{\Delta} Ca(HCO_3)_2$$

Effect of Heat on Bicarbonates

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$$
$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3 + H_2O + CO_2$$

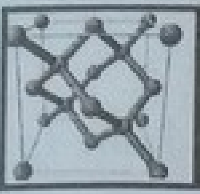
Effect of Heat on Nitrates

$$2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$$
$$4Li\,NO_3 \xrightarrow{\Delta} 2Li_2O + 4NO_2 + O_2$$
$$2Ca(NO_3)_2 \xrightarrow{\Delta} 2CaO + O_2 + 4NO_2$$

Role of Lime in Industries

⇒ $CaO + H_2O \longrightarrow Ca(OH)_2$
$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$
$Ca(OH)_2 + SiO_2 \longrightarrow CaSiO_3 + H_2O$

⇒ $CaO + C \longrightarrow CaC_2 + CO$
$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$



PRACTICE EXERCISE

30 mins Time Yourself

1. I – A elements are named as alkali metals because
   (a) Their oxides are basic
   (b) Their oxide and hydroxides are water soluble
   (c) Both 'a' & 'b'
   (d) They are found in earth
2. The word Alkali means
   (a) Base (b) Basic salt
   (c) Ashes (d) Spirit
3. Formula of Chile saltpetre is
   (a) $NaNO_3$ (b) $CaCO_3$
   (c) Ba $(NO_3)_2$ (d) NH_4Cl
4. The elements which are very abundant in earth crust are
   (a) Si & Aℓ (b) Ca & Mg
   (c) B & Aℓ (d) All
5. The oxides of beryllium BeO is
   (a) Acidic (b) Basic
   (c) Amphoteric (d) Neutral
6. Which element is necessary for normal leaf development?
   (a) Si (b) Ba
   (c) Mg (d) Ca
7. Li is different from its family members due to
   (a) small size (b) high charge density
   (c) less electropositivity (d) all of the above
8. Carbonates of lithium are not stable like that of sodium due to
   (a) Low electronegativity (b) Low electropositivity
   (c) Low charge density (d) Not known yet
9. Nitrates of which pair of elements give different products on thermal decomposition?
   (a) Na, K (b) Mg, Ca
   (c) Li, Na (d) Li, Ca
10. Which one of the following is not an alkali metal?
    (a) Francium (b) Caesium
    (c) Rubidium (d) Radium
11. Which of the following sulphates is not soluble in water?
    (a) Sodium sulphate (b) Potassium sulphate
    (c) Zinc sulphate (d) Barium sulphate
12. The element cesium bears resemblance with
    (a) Ca (b) Cr
    (c) Both of the above (d) None of the above
13. The ore $CaSO_4.H_2O$ has the general name
    (a) Gypsum (b) Dolomite
    (c) Calcite (d) Plaster of Paris

14. Down's cell is used to prepare
(a) Sodium carbonate
(b) Sodium bicarbonate
(c) Sodium metal
(d) Sodium hydroxide

15. Which element is produced at the cathode during the electrolysis of brine in Nelson's cell?
(a) H_2
(b) Na
(c) $C\ell_2$
(d) O_2

16. Ammonia may be prepared by heating ammonium chloride with
(a) Water
(b) NaCl
(c) Aqueous sodium hydroxide
(d) H_2SO_4

17. Calcium carbide is prepared by heating lime with coke at
(a) 2500°C
(b) 2600°C
(c) 2700°C
(d) 2800°C

18. Crystals of $Na_2CO_3.\ 10H_2O$ when exposed to air
(a) Lose water and remain solid
(b) Gain water and remain solid
(c) Gain water and become liquid
(d) Remains unchanged.

19. Which one of the following substances conducts electricity by the movement of ions?
(a) Graphite
(b) Copper
(c) Molten sodium chloride
(d) Mercury

20. Which one of the following gives white precipitate with aqueous solution of $BaC\ell_2$?
(a) $NaHCO_3$
(b) $NaNO_3$
(c) Na_2CO_3
(d) Na_2CrO_4

21. Which one of the following carbonate is water insoluble?
(a) Na_2CO_3
(b) K_2CO_3
(c) $(NH_4)_2CO_3$
(d) $CaCO_3$

22. The deliquescence is a property in which a solid
(a) Absorbs moisture and remains solid
(b) Absorbs moisture and turns to liquid form
(c) Loses water of crystallization
(d) Increases the number of water of crystallization.

23. In diaphragm cell, hydrogen is discharged by the reduction of
(a) Water
(b) HCl
(c) Na^+
(d) NaCl

24. In diaphragm cell, level of brine in anode compartment is kept slightly higher which prevents
(a) Hydroxide ions to reach anode
(b) Chlorine gas to mix
(c) Cathode to decay
(d) All of the above

25. Gypsum is applied to the soil as a source of
(a) Ca and P
(b) S and P
(c) Ca and S
(d) we could not apply

26. Alkali and alkaline earth metals impart colours when heated over burner. It is due to
(a) Smaller electronegativity of alkali metals
(b) Smaller ionic radius of these metals
(c) De-excitation of electrons from higher energy levels to low energy level
(d) Excitation of electrons from low energy levels to higher energy levels.

27. Which one of the following alkali metals forms only normal oxide when it reacts with O_2?
(a) Lithium
(b) Sodium
(c) Potassium
(d) Rubidium

28. First ionization potential of alkaline earth metal is greater than alkali metals because
(a) They are more reactive
(b) They have greater atomic radii
(c) They have smaller atomic sizes
(d) All

29. Which one of the following pairs shows diagonal relationship in the periodic table?
(a) Sodium and Lithium
(b) Lithium and magnesium
(c) Lithium and beryllium
(d) Boron and Beryllium

30. NaOH is named as caustic soda because
(a) It corrodes the organic tissues
(b) It is used in soda water
(c) It reacts with chlorine gas
(d) It reacts with fats to form soap

31. Sodium is not observed in +2 oxidation state because of its
(a) high first ionization potential
(b) high second ionization potential
(c) high ionic radius
(d) high electronegativity

32. Carnalite has chemical formula
(a) KCl
(b) $KCl.MgCl_2.6H_2O$
(c) $Na_2B_4O_7.10H_2O$
(d) $CaCO_3.MgCO_3$

33. Magnesium metal does not burn in the vessel containing
(a) N_2
(b) O_2
(c) N_2 and O_2
(d) Ne

34. Electrolysis of dilute solution of NaCl results at the anode
(a) sodium
(b) hydrogen
(c) chlorine
(d) oxygen

35. Second ionization potential of alkali metals are very high due to
(a) being s-block elements
(b) inert gas configurations
(c) ns^1 electronic configuration
(d) being metals

36. Which ion will have maximum value of heat of hydration?
(a) Al^{+3}
(b) Cs^+
(c) Ba^+
(d) Mg^{+2}

37. Which one can form complex?
(a) Na
(b) Cr
(c) Li
(d) K

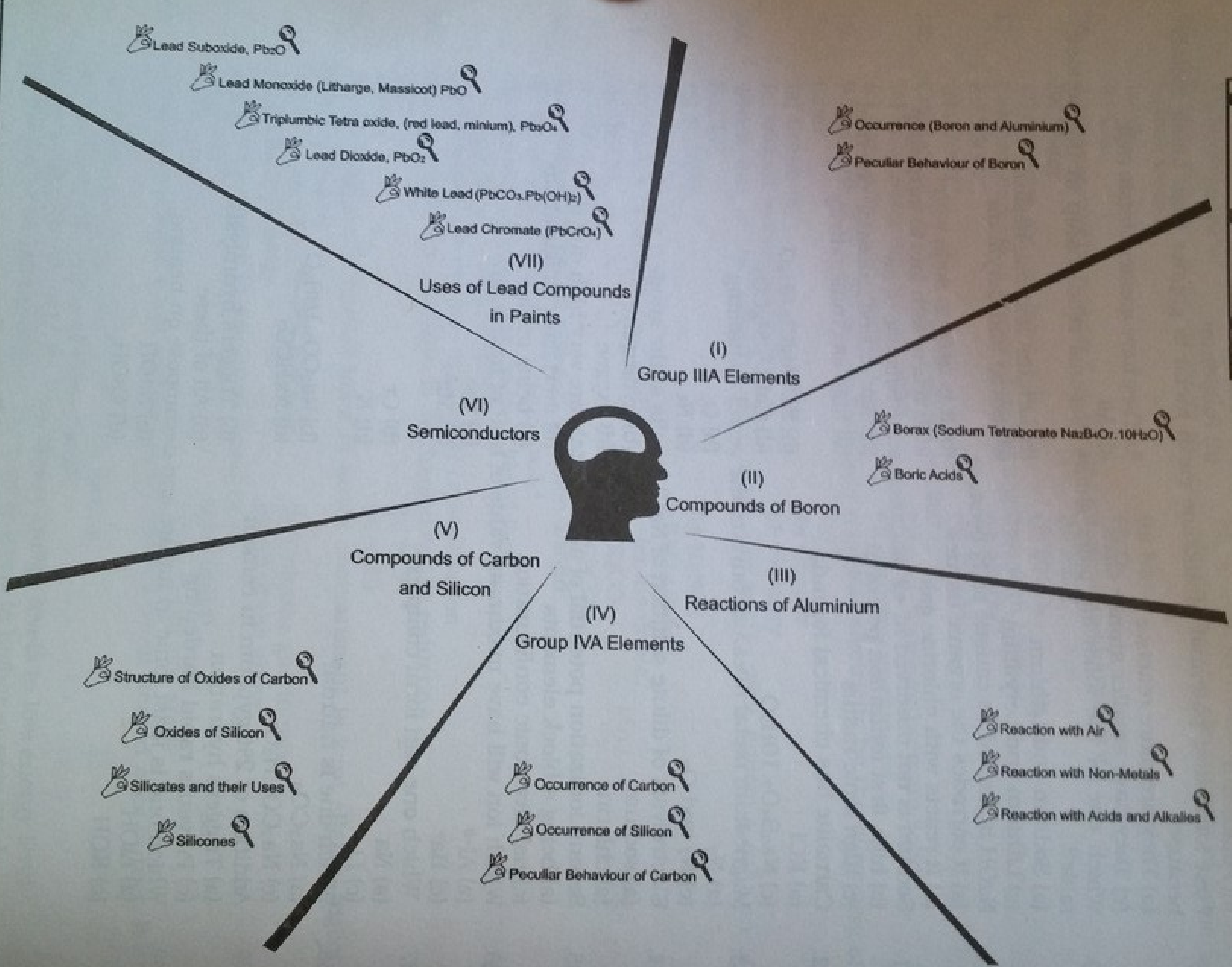
38. Which one is natron?
(a) Na_2CO_3
(b) $Na_2CO_3.10H_2O$
(c) $Na_2CO_3.H_2O$
(d) $NaHCO_3$

39. Addition of 2% gypsum in cement
(a) Triggers hydration
(b) Triggers hydrolysis
(c) Prevents rapid hardening
(d) All of these

40. Which one is least ionic in nature and decompose on heating.
(a) LiOH
(b) NaOH
(c) KOH
(d) CsOH

Chapter 3

GROUP IIIA & IVA ELEMENTS



(I)
Group IIIA Elements

- Occurrence (Boron and Aluminium)
- Peculiar Behaviour of Boron

(II)
Compounds of Boron

- Borax (Sodium Tetraborate $Na_2B_4O_7.10H_2O$)
- Boric Acids

(III)
Reactions of Aluminium

- Reaction with Air
- Reaction with Non-Metals
- Reaction with Acids and Alkalies

(IV)
Group IVA Elements

- Occurrence of Carbon
- Occurrence of Silicon
- Peculiar Behaviour of Carbon

(V)
Compounds of Carbon and Silicon

- Structure of Oxides of Carbon
- Oxides of Silicon
- Silicates and their Uses
- Silicones

(VI)
Semiconductors

(VII)
Uses of Lead Compounds in Paints

- Lead Suboxide, Pb_2O
- Lead Monoxide (Litharge, Massicot) PbO
- Triplumbic Tetra oxide, (red lead, minium), Pb_3O_4
- Lead Dioxide, PbO_2
- White Lead ($PbCO_3.Pb(OH)_2$)
- Lead Chromate ($PbCrO_4$)

Chapter 3

Group IIIA & IVA Elements

GROUP IIIA ELEMENTS

Group IIIA of the periodic table consists of five elements as boron (B), aluminium (Al), gallium (Ga), indium (In) and thallium (Tl).

GENERAL TREND OF IIIA GROUP

Elements of III-A
• Metallic character increases down the group • B is non metal others are metals. • p-atomic orbital is in the process of completion • Lesser shielding effect • Elements show +3 oxidation state. • Elements give normal oxides • Gives halides MX_3 • Al is present as Aluminosilicates • Gallium, Indium and Thallium are rare elements

OCCURRENCE OF BORON

Boron is always found in nature combined with oxygen usually as oxyborate ions and salts of various polyboric acids.

Element	Name of mineral	Chemical formula
Boron	Borax or tincal	$Na_2B_4O_7.10H_2O$
	Colemanite	$Ca_2B_6O_{11}.5H_2O$
	Orthoboric acid	H_3BO_3

PECULIAR BEHAVIOUR OF BORON

Boron	Other elements of III-A
Only non metallic with less than four valence electrons.	Metallic
Boron has oxidation state +3,-3	Other elements has +3
Molecular addition compounds are formed	No reaction
Does not form ionic compound	Formation of ionic compound
It forms acidic oxides.	Amphoteric oxides except Tl
It can form acids like HBO_2, H_3BO_3 etc.	Do not form.

COMPOUNDS OF BORON

BORAX($Na_2B_4O_7.10H_2O$)

- Present as natural deposit called **tincal** after drying of lake.
- Lakes are present in Tibet and California.

PREPARATION OF BORAX

Detail of reaction	Chemical formula	Remarks
From boric acid and soda ash	▪ $4H_3BO_3 + Na_2CO_3 \rightarrow Na_2B_4O_7 + 6H_2O + CO_2$	▪ It is an old method ▪ Hot solution of boric acid is used
From calcium borate	▪ $Ca_2B_6O_{11} + 2Na_2CO_3 \rightarrow 2CaCO_3 + Na_2B_4O_7 + 2NaBO_2$ ▪ $NaBO_2 + CO_2 \rightarrow Na_2CO_3 + Na_2B_4O_7$	▪ It is a modern method ▪ Solution of borax and sodium metaborate leave to crystallize borax ▪ To get more borax, add CO_2 gas
From tincal	–	▪ Tincal is dissolved in water ▪ Evaporation is carried out ▪ Crystal of borax will separate out.

PROPERTIES OF BORAX

- Solubility is 3g/100g water at 10°C
- Solubility is 99.3g/100g water at 100°C
- Above 62°C, pentahydrated octahedral crystals exist
- Below 62°C, decahydrated monoclinic crystals exist
- Borax Bead Test is conducted through heating of borax
- Reaction with acids like HCl and H_2SO_4 gives boric acid
- Reaction with NH_4Cl gives boron nitride
- Solution of borax is alkaline in nature

USES OF BORAX

- Preparation of borate glass (heat resistant).
- Water softening agent.
- Detection of coloured metallic cations (Borax Bead Test).
- Metallurgy
- Welding flux
- Leather industry for tanning & dying.
- Cosmetic, soap, textiles, paints, medicines, match industry and as preservative of food.

BORIC ACIDS

- Formulas of four boric acids are as follows:
  a) Orthoboric acid, H_3BO_3 or $B_2O_3.3H_2O$
  b) Meta boric acid, HBO_2 or $B_2O_3.H_2O$
  c) Tetra boric acid, $H_2B_4O_7$ or $2B_2O_3.H_2O$
  d) Pyroboric acid, $H_6B_4O_9$ or $2B_2O_3.3H_2O$

ORTHOBORIC ACID

- Orthoboric acid is stable, while others are stable only in solid form.
- Others change into ortho form in aqueous solution.
- Crystal of orthoboric acid is triclinic.
- It is sparingly soluble in cold water (2.6% at 40°C) but more soluble in warm water (37% at 107°C).

PROPERTIES OF BORIC ACID (H_3BO_3)

Particulars	Reaction Involved	Remarks
Physical appearance	-	Crystalline solid, soft, soapy touch.
Solubility	-	Fairly soluble in water (cold)
Effect of steam	-	Become volatile
Reaction with C_2H_5OH	$H_3BO_3+C_2H_5OH \rightarrow (C_2H_5)_3BO_3+H_2O$	-
Effect of heat	$H_3BO_3 \rightarrow HBO_2$ (metaboric acid) $HBO_2 \rightarrow H_2B_4O_7$ (tetraboric) $H_2B_4O_7 \rightarrow B_2O_3$(Boric anhydride)	Loss of water
Acidic behaviour	$H_3BO_3+H_2O \rightarrow [B(OH)_4]^-+H^+$	Monobasic Lewis acid
Effect on litmus paper		▪No effect on methyl orange ▪Turns blue litmus to red.
Effect of NaOH	$H_3BO_3+NaOH \rightarrow Na_2B_4O_7+H_2O$	▪Partially neutralized ▪Borax is produced
Titration with alkali		▪No titration in normal condition ▪Titrated in presence of glycerol ▪Phenolphthalein is an indicator

ALUMINIUM

Occurrence

Element	Name of mineral	Chemical formula
Aluminium	Feldspar	$KAlSi_3O_8$
	Mica (Muscovite)	$KH_2Al_3(SiO_4)_3$
	Kaoline	$Al_2O_3.2SiO_2.2H_2O$
	Corundum	Al_2O_3
	Emerald	$Al_2F_2SiO_4$
	Gibbsite	$Al_2O_3.3H_2O$
	Bauxite	$Al_2O_3.2H_2O$
	Cryolite	Na_3AlF_6
	Diaspore	$Al_2O_3.H_2O$

REACTION OF ALUMINIUM

Particulars	Chemical reaction	Remarks
Reaction with H_2	$2Al+3H_2 \rightarrow 2\ AlH_3$	
Reaction with O_2	$2Al+3O_2 \rightarrow 2\ Al_2O_3$	▪Intense light is produced ▪Used in flash light photography ▪When burnt in air, AlN is produced.
Reaction with N_2	$Al+N_2 \rightarrow AlN$	This reaction is used in removing of air bubbles in molten metals ▪Salt solution corrode aluminium and aluminium alloys badly, so are not suitable for marine use.
Reaction with X_2	$2Al+X_2 \rightarrow 2AlX_3$	Exothermic
Action of acids	▪ $2Al+6HCl \rightarrow 2AlCl_3+3H_2$ ▪ $2Al+6H_2SO_4 \rightarrow Al_2(SO_4)_3+3SO_2+6H_2O$ ▪ $Al + HNO_3 \rightarrow x$	▪H_2 is evolved with reaction of dil. acid ▪On reaction with conc. H_2SO_4, SO_2 is evolved
Action of alkali	▪ $2Al+2NaOH+6H_2O \rightarrow 2NaAl(OH)_4+3H_2$	Al is dissolved in alkali forms soluble sodium aluminate and liberates H_2

USES

1- Aluminium is very light and is used in the construction of air crafts ships and cars.
2- Due to its conductivity, it is used in a manufacture of heavy duty electrical cables.
3- Due to its reflection power it is commonly used to insulate buildings.
4- It is non magnetic and is thus used in navigational equipment.
5- It is non-toxic and can be used for making food and brewing equipments and in packaging.
6- Aluminium readily forms alloys with other metals like copper, magnesium, nickel and zinc.
7- At homes, aluminium is found in the form of cooking utensils, window frames and kitchen foil.
8- Aluminium is used for making petrol and milk storage tanks because it reflects heat and prevents them of being over heated in the sun.
9- Aluminium is excellent reflector of radiation and energy.
10- It is good reducing agent.

IVA GROUP

Group IVA of the periodic table consist of five elements including carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb).

Common Properties of Group IVA Elements

1- All the elements of this group show a valency of four except tin and lead which either show four or two valency. Two due to inert pair effect.
2- All of them form hydrides, XH_4.
3- They form tetrachlorides, XCl_4.
4- They also form the dioxides, XO_2.

CARBON

Occurrence of Carbon

Carbon can be found in free and combined state.

Element	Name of Ore	Chemical formula
Carbon	Limestone	$CaCO_3$
	Dolomite	$MgCO_3.CaCO_3$
	Magnesite	$MgCO_3$

Uniqueness Of Carbon

1- Carbon and silicon are nonmetals while the other members of the family are metalloids (Ge,Sn) or metals (Pb).
2- Carbon shows the property of catenation or self linkage markedly.
3- Tetravalent can combine with four same or different elements.
4- Can form multiple bonds.
5- Carbon also forms homocyclic and heterocyclic compounds.

Oxides of Carbon

There are three oxides of carbon

a. CO
b. CO_2
c. C_3O_2 (carbon suboxide)

STRUCTURE OF CO AND CO_2

CO_2	CO
Molecule is linear	Molecule is almost linear
Dipole moment is zero	Dipole moment is 0.112D.
All electrons of C-atom take part in bond formation	Two valence electrons are inert in C and two form covalent bonds.
σ and π bonds are present	σ and π bonds are present
Co-ordinate covalent bond is absent	Co-ordinate covalent bond is present
Used in soft drinks and fire extinguishers.	Toxic and form carboxy haemoglobin complex in blood.

SILICON

It occurs only in combined state.

Element	Name of material	Chemical formula
Silicon	Analcite (a zeolite)	$NaAl(SiO_3)_2.H_2O$
	Asbestos	$CaMg_3(SiO_3)_4$
	Kaolin (pottery clay)	$H_2Al_2(SiO_4)_2.H_2O$
	Zircon	$ZrSiO_4$
	Talc (soap stone)	$H_2Mg_3(SiO_3)_4$

COMPOUNDS OF SILICON

- Silica
- Silicates
- Silicones

SILICON DIOXIDE (SiO_2)

- Every Si atom is tetrahedrally attached with four O atoms.
- Each oxygen atom is attached to two silicones.
- Ratio of atoms Si and O is 1:2

QUARTZ

- Quartz, the common crystalline form of silicon oxide, is a hard, brittle, refractor, colourless solid which differs very markedly from carbon dioxide.
- Quartz is found in the following forms:_Rock crystal, amethyst quartz, smoky quartz, rose quartz, milky quartz. Opal is hydrated variety of quartz. Sand is largely silicon dioxide (silica).

VITREOUS SILICA/ SILICA GLASS (Incorrectly called fused quartz)

- On heating at high temperature, it gives viscous liquid
- On cooling, it becomes rigid without going into a regular crystal pattern.

INTERESTING & USEFUL PROPERTIES OF VITREOUS SILICA

- High transparency to light
- Can withstand very high temperature i.e. 1500°C-1600°C
- Very low thermal expansion
- Excellent insulator
- Hard brittle and elastic
- Insoluble in water and inert with other reagents
- Inert towards acids except HF.

COMPARISON OF CO_2 AND SiO_2

CO_2	SiO_2
Double covalent bonds are present	Single covalent bonds are present
C atom is smaller	Si atom is larger
Molecule is linear	Tetrahedral geometry is present
Structure is one dimensional	Structure is three dimensional

SILICATES

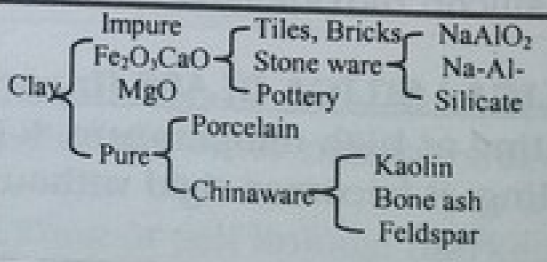
The compounds derived from silicic acid are termed as silicates.

SODIUM SILICATE (Na_2SiO_3)

- It is a sodium salt of metasilicic acid
- It is also called water glass or soluble glass
- Prepared by Na_2CO_3 and pure sand.
- Soluble in water and its solution is alkaline
- When soluble colored salts like $NiCl_2$, $FeSO_4$ and $CuSO4$ are dissolved in solution of water glass, they give beautiful growth called chemical garden.

ALUMINIUM SILICATES or CLAY

- Aluminium is present in important silicate rocks
- Weathering effect, effect of CO_2 and effect of H_2O (freezing and melting) disintegrate the silicate rocks into clay.
- Pure clay "$Al_2O_3.(SiO_2)_2\,2H_2O$" also called kaolin used in preparation of porcelains and china wares.
- Ordinary clay contains Fe and it is of yellow or reddish yellow.
- Ordinary clay is used to prepare bricks, tiles and stone wares.

S.No	Name and Formula of Silicates	Preparation	Properties	Uses
1	Sodium Silicate Na_2SiO_3	$Na_2CO_3+S_iO_2 \longrightarrow Na_2SiO_3+CO_2$ $2NaOH+H_2SiO_3 \longrightarrow Na_2SiO_3+2H_2O$	Aqueous Solution	Soap – Filler Textile – Fireproof Furniture – Polish Calico – Printing Chemical Garden
2	Aluminum Silicate $Al_2O_3.(SiO_2)_2.2H_2O$	$K_2O.Al_2O_3.6SiO_2+H_2CO_3+H_2O \longrightarrow K_2CO_3+{}^4SiO_2+Al_2O_3.(SiO_2)_2.2H_2O$ Kaolin	 Clay Impure Fe_2O_3CaO MgO Tiles, Bricks Stone ware Pottery $NaAlO_2$ Na-Al-Silicate Pure Porcelain Chinaware Kaolin Bone ash Feldspar	
3	Talc/Soap Stone $H_3Mg_3(S_iO_3)_4$		Greasy Touch	Cosmetics House hold Articles
4	Asbestos $CaMg_3(S_iO_3)_4$		Hydrated Mg Silicate	Incombustible Fabrics Hard Board

SILICONES:

The compound in which Si is surrounded by two O atoms and wo alkyl groups is called silicone

- Chemistry of silicone is similar to carbon
- Forms SiO_2, $SiCl_4$ and Silane (SiH_4) like C.
- Silicones are very inert to oxygen at high temperature.
- Its viscosity is not affected by the change in temperature.
- Silicones are used:
  - ™ in preparation of lubricants
  - ™ in hydraulic brakes or hydraulic system
  - ™ methyl silicones of high molecular mass resemble rubber and are used in making rubber like tubing and sheets.
  - ™ due to presence of cross linkages, in insulation
  - ™ silicone films can prevent water leakage and act as water repellent like a grease film.

SEMICONDUCTORS

Substance having different resistances to the passage of electric current is called semiconductor

- Compounds/elements acts as semiconductor are Germanium, Selenium, Silicones, Lead sulphide, Silicon carbide, Calcium sulphide, Lead telluride, Gallium arsenide, Indium antimonide.
- Electrical conductance depends upon temperature of semiconductor.
- On heating resistance of semiconductor decrease while that of metal increases.
- In light conductance of semi conductor increases
- Semi conductors are used in transistors, photoelectric cell and solar batteries.
- The junction between the different materials forms a boundary. It allows electricity to pass more properly and is used in transistors.

USE OF LEAD COMPOUNDS

Compound	Remarks	Uses
Lead Compounds		as pigment
Lead suboxide (Pb_2O)	▪ It is a black powder	in lead storage batteries as filler
Lead monoxide (PbO)	▪ Two crystalline forms are available: 1. rhombic(yellow in colour) 2. tetragonal(red in colour) ▪ it is slightly soluble in water	▪ in preparing flint glass and paints
Triplumbic tetra-oxide (Pb_3O_4)	▪ It is produced after the action of O_2 and Pb	▪ in preparation of storage batteries ▪ in anticorrosion paint.
Lead oxide (PbO_2)	▪ It is produced after the reaction of HNO_3 and red lead ▪ It is reddish brown powder ▪ It is soluble in alkaline water ▪ Unaffected by dilute acids.	▪ forms plumbates
White lead $2PbCO_3.Pb(OH)_2$	▪ It is amorphous white pigment. ▪ Prepared by Dutch process.	▪ has good covering power when mixed with lin seed oil ▪ toxic and tarnished to grey by environment.

PRACTICE EXERCISE

20 mins Time Yourself

1. Boron is non-metal whereas Al is metal, it is due to
   (a) Small size (b) High nuclear charge
   (c) Both a and b (d) No authorized justification yet
2. Boron in soil has been considered micronutrient for
   (a) Soil porocity (b) Proper growth of plants
   (c) Alkalinity of soil (d) All
3. One of the outstanding features of boron is its ability to form
   (a) Molecular addition compounds (b) Molecular crystals
   (c) Semiconductors (d) Ionic compounds
4. Substance which is found in dried up lakes of Tibet and California is
   (a) Tincal (b) Boric acid
   (c) Calcium carbonate (d) Colemanite
5. Borax is a white crystalline solid and it is
   (a) More soluble in cold water (b) More soluble in hot water
   (c) Insoluble in water (d) Soluble only in organic solvents
6. Which of the following does not give Borax bead test?
   (a) Cu (b) Cr
   (c) Ni (d) Al
7. Special features of borate glass is that it is
   (a) Heat resistant (b) Low melting
   (c) Used to prepare chemical garden (d) Green in colour
8. The metal which is used in thermite process because of its activity, is
   (a) iron (b) copper
   (c) aluminium (d) zinc
9. Aluminium oxide is
   (a) Acidic oxide (b) Basic oxide
   (c) Amphoteric oxide (d) It does not exists
10. Which of the following shows inert pair effect?
    (a) boron (b) carbon
    (c) silicon (d) tin
11. Which electronic configuration corresponds to an element of group IIIA?
    (a) $1s^2,2s^2,2p^3$ (b) $1s^2,2s^2,2p^6,3s^2,3p^1$
    (c) $1s^2,2s^2,2p^4$ (d) $1s^2,2s^2,2p^6,3s^2,3p^6,4s^2,3d^1$
12. Tincal is a mineral of
    (a) Al (b) Si
    (c) B (d) C
13. In network of silica (SiO_2), each silicon atom is surrounded by ________ atoms of oxygen
    (a) 4 (b) 2
    (c) 1 (d) 6
14. Which one of the following is not a semiconductor?
    (a) Si (b) Ge
    (c) Se (d) Sn

15. Orthoboric acid is 2.6% soluble in water at 40°C and ______ at 107°C.
(a) 26%
(b) 27%
(c) 37%
(d) < 2.6%

16. The process of aluminium extraction is called
(a) Hall process
(b) Thermite process
(c) Haber process
(d) Contact process

17. Because of its ability to combine with both oxygen and nitrogen, aluminium metal is used
(a) As nitrometer
(b) To remove air bubbles from molten metal
(c) To produce alloy
(d) As insulator

18. Aqueous solution of borax above 62°C gives crystals of
(a) $Na_2B_4O_7.4H_2O$
(b) $Na_2B_4O_7.5H_2O$
(c) $Na_2B_4O_7.2H_2O$
(d) $Na_2B_4O_7.10H_2O$

19. Silicon differ from silica by a group of
(a) CH_3
(b) -OH
(c) OCH_3
(d) O_2

20. Which of the following is not a use of silicon?
(a) Lubricants
(b) Hydraulic brakes
(c) Antifreeze
(d) Water repellent

21. Boron is non metal while other elements of IIIA group are metals. This is because
(a) it has small size
(b) it has high nuclear charge
(c) it forms molecular addition compounds
(d) all of the above

22. CO_2 is gas while SiO_2 is solid at room temperature.
(a) carbon is non-metal while silicon is semi-metal
(b) CO_2 is an independent molecule while SiO_2 has network covalent structure
(c) CO_2 forms multiple bond while silicon does not form multiple bonds
(d) Silicon has all sigma bonds.

23. The coloured glassy mass in borax bead test is due to the formation of
(a) metal borate
(b) metal meta borate
(c) metal boride
(d) metal silicate

24. Identify the correct statement regarding CO
(a) it combines with H_2O to form carbonic acid
(b) it reacts with red blood cells of haemoglobin
(c) it is powerful oxidizing agent
(d) it is used to prepare aerated drinks.

25. The chief ore of Aℓ is:
(a) $Na_3A\ell F_6$
(b) $A\ell_2O_3\ 2H_2O$
(c) $A\ell_2O_3\ H_2O$
(d) $A\ell_2O_3\ 3H_2O$

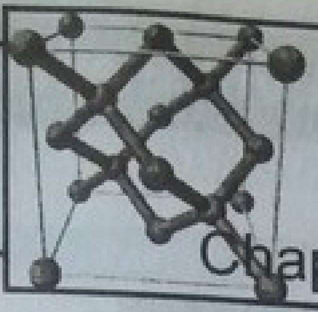
26. If temperature of gallium arsenide is increased then its conductivity will
(a) decrease
(b) increase
(c) remains constant
(d) first decreases then increases

27. Boric acid cannot be used
(a) As antiseptic in medicine
(b) For washing eyes
(c) In soda bottles
(d) For enamel and glazes.

28. Which of the following will decompose to produce litharge
(a) Pb_2O
(b) Pb_3O_4
(c) PbO_2
(d) All of the above

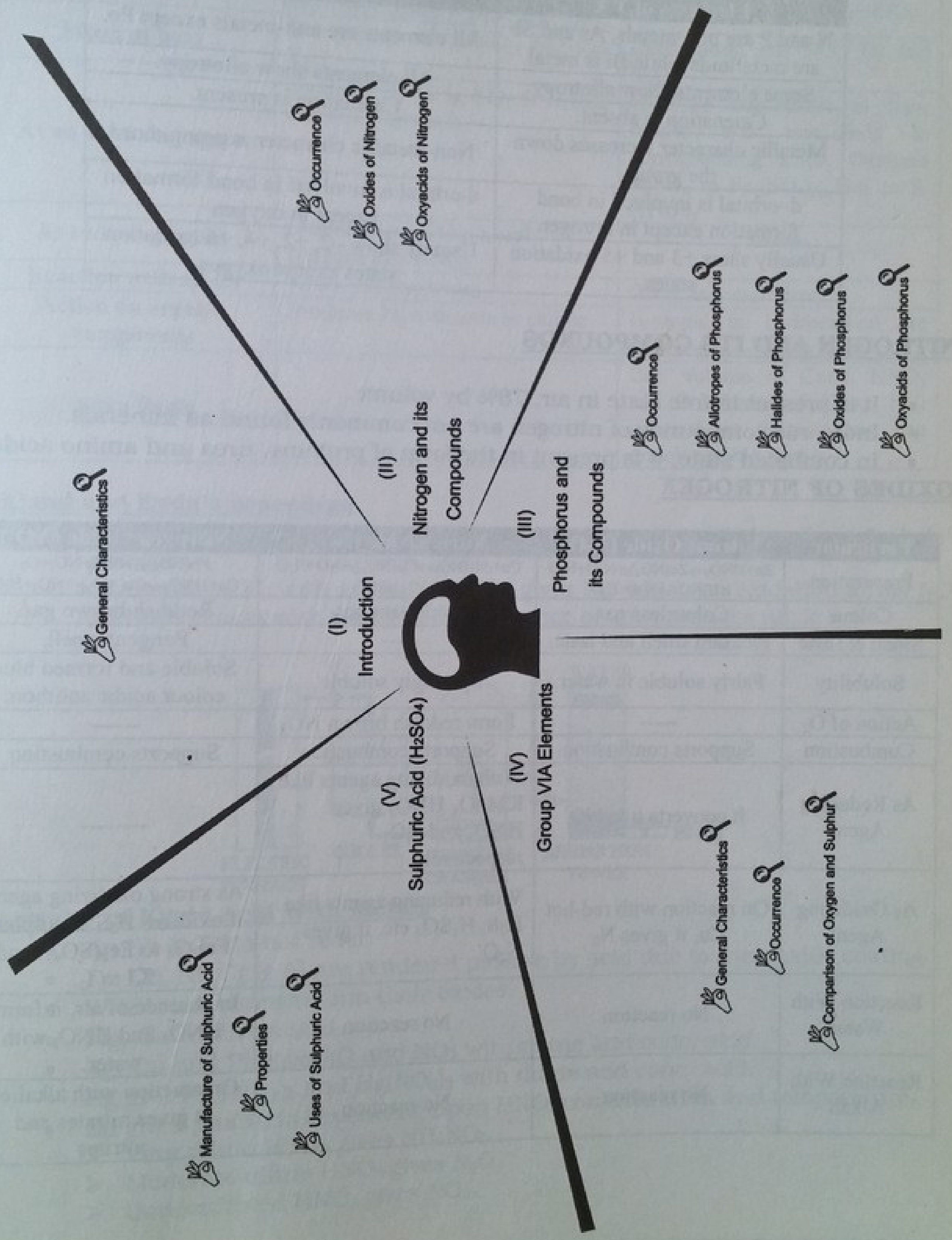
29. Which element can form tripositive ion?
(a) Beryllium
(b) Carbon
(c) Silicon
(d) Aluminium

30. Which of the following is metasilicic acid?
(a) H_2SnO_3
(b) H_2SiO_3
(c) H_3AsO_4
(d) H_3SbO_4



Chapter 4

GROUP VA & VIA ELEMENTS



INTRODUCTION

Elements of VA	Elements of VIA
N and P are non-metals, As and Sb are metalloids while Bi is metal.	All elements are non-metals except Po.
Some elements show allotropy.	All elements show allotropy.
Catenation is absent.	Catenation is present.
Metallic character increases down the group.	Non-metallic character is pronounced
d–orbital is involved in bond formation except in nitrogen	d-orbital is involved in bond formation except in oxygen
Usually show +3 and +5 oxidation states.	Usually show –2, +2, +4, +6 oxidation states except oxygen.

NITROGEN AND ITS COMPOUNDS

- It is present in free state in air, 78% by volume.
- Inorganic compounds of nitrogen are not commonly found as minerals.
- In combined state, it is present in the form of proteins, urea and amino acids.

OXIDES OF NITROGEN

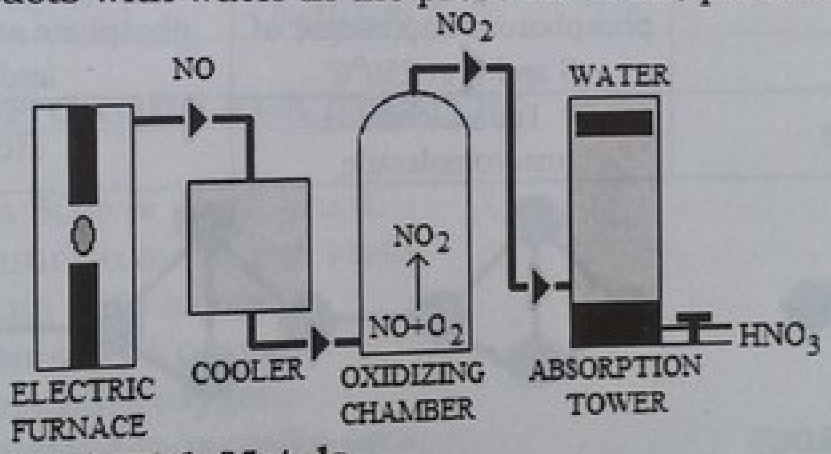
Particular	Nitrous Oxide (N_2O)	Nitric Oxide (NO)	Nitrogen Oxide (NO_2)
Preparation	$Zn+HNO_3 \rightarrow Zn(NO_3)_2+N_2O+H_2O$ $NH_4NO_3 \rightarrow N_2O+H_2O$	$Cu+dilHNO_3 \rightarrow Cu(NO_3)_2+NO+H_2O$ $N_2+O_2 \rightarrow 2NO$	$Pb(NO_3)_2 \rightarrow PbO+NO_2+O_2$ $Cu+HNO_3 \rightarrow Cu(NO_3)_2+NO_2+H_2O$
Colour	Colourless gas.	Colourless gas.	Reddish brown gas.
Smell &Taste	Pleasant smell and taste.	-----	Pungent smell.
Solubility	Fairly soluble in water.	Sparingly soluble.	Soluble and formed blue colour acidic solution.
Action of O_2	-----	Form reddish brown NO_2	------
Combustion	Supports combustion	Supports combustion	Supports combustion
As Reducing Agent	It converts into NO	With oxidizing agents like $KMnO_4$, HNO_3 gives HNO_3 and NO_2 respectively.	--------
As Oxidizing Agent	On reaction with red-hot Cu, it gives N_2.	With reducing agents like H_2S, H_2SO_4 etc, it gives N_2O.	As strong oxidizing agent, it oxidizes H_2S to sulphur, $FeSO_4$ to $Fe_2(SO_4)_3$ and KI to I_2.
Reaction With Water	No reaction	No reaction	In absence of air, it forms HNO_3 and HNO_2 with water.
Reaction With Alkali	No reaction	No reaction	On reaction with alkalies, it gives nitrates and nitrites

ACIDS OF NITROGEN

Particulars	Nitrous acid (HNO_2)	Nitric acid(HNO_3)
Preparation	$N_2O_3+H_2O \rightarrow HNO_2$ $Ba(NO_2)_2+H_2SO_4 \rightarrow BaSO_4+HNO_2$	$KNO_3+H_2SO_4 \rightarrow KHSO_4+HNO_3$
Effect of heat	Decompose into HNO_3, NO and H_2O	Decompose into NO_2, O_2 and H_2O
As an oxidizing agent	Oxidizes HI to I_2, SO_2 to H_2SO_4 and $SnCl_2$ to $SnCl_4$	Oxidizes non-metals to their oxides and metalloids to corresponding acids. Oxidizes $FeSO_4$ to $Fe_2(SO_4)_3$, H_2S to S, HI to I_2
As reducing agent	Decolourizes $KMnO_4$ and changes into HNO_3	--------
Reaction with alkali	Gives salt and water	Gives salt and water
Action on organic compounds	Produces N_2 with urea or aniline.	H-atoms in hydrocarbon are replaced by $-NO_2$ group
Aqua Regia		One volume of Conc. HNO_3 and 3 volume of Conc. HCl give Aqua Regia that can dissolve noble metals

Brikland and Eyde's procedure

- Another method for preparation of nitric acid is Birkland and Eyde's process.
- Oxidation of N_2 with atmospheric O_2 gives NO which on oxidation forms NO_2 and this reacts with water in the presence of air, produces nitric acid.



Reactivity of Nitric Acid With Metals

- Au, Pt & Ti do not react.
- Fe, Co, Ni, Cr & Al are rendered passive by acid due to their oxide coating.
- W & U are changed into their oxides.
- Mg, Ca & Mn gives H_2.
- Ag, Cu and Pb give NO and NO_2 with dilute and conc. acid.
- Hg give $Hg_2(NO_3)_2$ and $Hg(NO_3)_2$ with dilute and conc. acid.
- Zn gives products depending upon HNO_3 concentration and temperature.
  - ➢ Very dilute HNO_3 gives NH_4NO_3.
  - ➢ Moderate dilute HNO_3 gives N_2O.
  - ➢ Concentrated HNO_3 gives NO_2.

PHOSPHORUS AND ITS COMPOUNDS

OCCURRENCE OF PHOSPHORUS

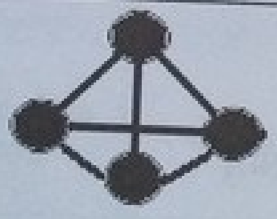
- Phosphorus is found in combined state in the form of minerals.
- It is present in seed, yolk of eggs, nerves, brain and bone marrows.
- Bone ash [80% $Ca_3(PO_4)_2$] is source of P.

ALLOTROPES OF PHOSPHORUS

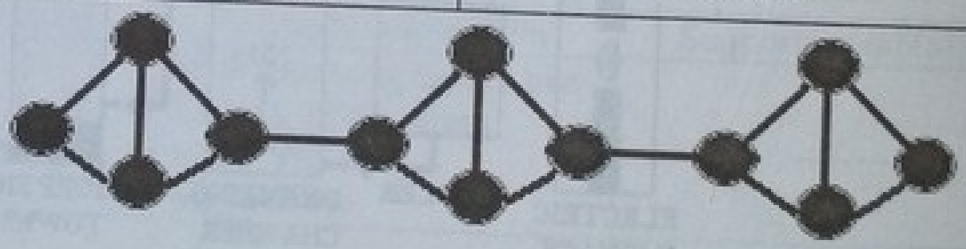
Different crystalline forms of any substance are said to be allotropes. There are six allotropes of phosphorous;

1. Yellow/ White Phosphorous
2. Red Phosphorous
3. Scarlet Phosphorous
4. α-Black Phosphorous
5. β-Black Phosphorous
6. Violet Phosphorous

White Phosphorus	Red Phosphorus	Black Phosphorus
Very reactive, poisonous, volatile, waxy and yellowish.	Less reactive and poisonous.	-
Soluble in C_6H_6 and CS_2	-	-
Exist in tetra atomic form	Tetra atomic form	-
Change into P_2 at 700°C	-	-
-	Prepared by heating white phosphorous in presence of S and I_2 at 250°C	Prepared by heating red phosphate at high temperature and pressure
Tetrahedral in shape	Tetra-atomic macromolecule	Hexagonal



WHITE PHOSPHOROUS



RED PHOSPHOROUS

HALIDES OF PHOSPHORUS

Particulars	PCl_3	PCl_5
Colour	Colourless liquid	Yellowish crystal
Boiling point	76°C	Sublims at 100°C
Freezing point	-112°C	-
Effect of heat	-	Changes into Cl_2 and PCl_3
Action of O_2	Phosphorus oxychloride is produced	-
Action of water	Forms phosphorous acid	Forms orthophosphoric acid
Action of alcohol	Forms alkyl chloride and phosphorous acid	Forms alkyl chloride and phosphorus oxychlorides

OXIDES OF PHOSPHOROUS

Particulars	Phosphorous trioxide	Phosphorus pentaoxide
Smell and state	White waxy solid and garlic smell	White powder and garlic like smell
Melting point	22.8°C	Sublimes at 360°C
Boiling point	173°C	-
Action of Oxygen	Changes into P_2O_5	-
Action of water	• With cold water, gives phosphorus acid • With hot water, gives phosphoric acid and phosphene gas	Forms meta phosphoric acid

ACIDS OF PHOSPHORUS

Particulars	Phosphorus acid(H_3PO_3)	Phosphoric acid (H_3PO_4)
Colour and state	White crystalline solid	Colourless deliquescent crystalline solid
Melting point	73.6 °C	41°C
Effect of heat	Changes into phosphine and phosphoric acid	Changes into pyro and metaphosphoric acid $2H_3PO_4 \rightarrow H_4P_2O_7 \rightarrow 2HPO_3$
Action with O_2	Gives phosphoric acid	-
Action with alkali	Forms salts	Forms salts
As reducing agent	Reduces $CuSO_4$ to Cu and $AgNO_3$ to Ag	-

OCCURRENCE OF GROUP VI-A ELEMENT

- O_2 comprises 50% of earth crust.
- Oxygen is found in air in free state
- Water contains 89% oxygen.
- $CaCO_3$ contains 48% oxygen.
- Silica contains 53% oxygen.
- Sulphur is present in metallic ores.
- Sulphur is also present in onions, garlic, mustard, hair, oil, egg & proteins.

MINERALS OF GROUP VIA ELEMENTS

Name	Formula
Galena	PbS
Zinc blend	ZnS
Cinnabar	HgS
Stibnite	Sb_2S_3
Copper pyrite	Cu_2S
Iron pyrite (Fool's Gold)	FeS_2
Gypsum	$CaSO_4.2H_2O$
Heavy spar	$BaSO_4$

COMPARISON OF OXYGEN AND SULPHUR

SIMILARITIES BETWEEN OXYGEN AND SULPHUR
➢ Both have same Outer shell Electronic configuration i.e. ns^2np^4
➢ Both are usually divalent
➢ Both show allotropy
➢ Both have polyatomic molecules.
➢ Both combine with metals with oxidation state -2.
➢ Both combine with non-metals and form covalent compounds.
➢ Both are found in both free and combined states.
➢ Both are typical non-metals.

DIFFERENCES

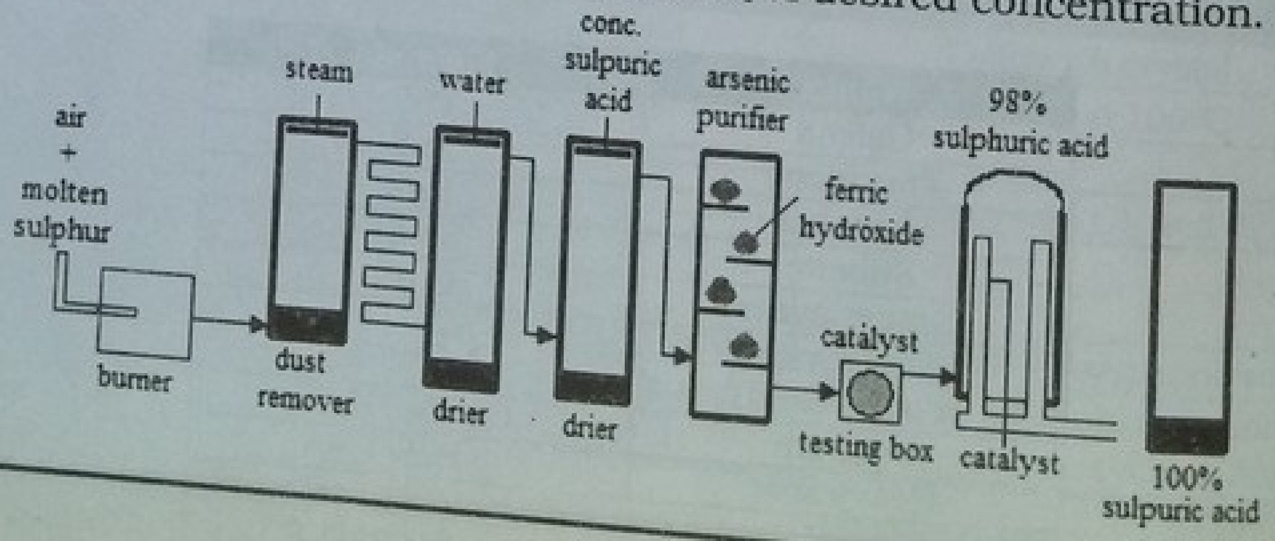
Oxygen	Sulphur
Two allotropic forms O_2 & O_3	Three allotropic forms rhombic, monoclinic & plastic.
Gas at ordinary temperature.	Solid at ordinary temperature.
Sparingly soluble in water	Insoluble in water
Helps in combustion.	It is itself combustible.
Does not react with water.	Boiling sulphur reacts with steam producing a little hydrogen sulphide & sulphur dioxide.
Does not react with acids.	Readily oxidized by conc. Sulphuric acid & nitric acid.
Does not react with alkalies.	Reacts with alkali solution & forms sulphides & thiosulphate.
It shows -2,-1,-1/2,+2oxidation states.	It shows -2, +2, +4 and +6 oxidation states
It is paramagnetic.	It is diamagnetic.

SULPHURIC ACID (H_2SO_4)

- Discovered by **Jabar-Ibn-Hayan**
- It was called **oil of vitriol.**

Contact Process

- SO_2 is produced by burning of S or FeS_2 and again oxidized to SO_3 in the presence of air and V_2O_5 at 400-500°C in contact chamber.
- SO_3 absorbed by H_2SO_4 and converts into Oleum $H_2S_2O_7$.
- Water is added to $H_2S_2O_7$ and forms H_2SO_4 of desired concentration.



Properties of H_2SO_4

- Colourless oil liquid
- Specific gravity is 1.834 at 18°C
- Freezing point 10.5°C
- Boiling point 338°C
- Soluble in water, exothermic reaction
- Pure is nonconductor, but addition of a little water makes it good conductor.
- Corrosive to skin and causes very serious burn to all tissues.

Chemical Properties

- On heating changes into SO_3 and H_2O
- Strong acid completely ionizes in water
- Reacts with alkali to give salt and water
- Reacts with carbonates and bicarbonates to give salt
- Reacts with NH_3 to give ammonium sulphate
- Reacts with benzene to give benzene sulphonic acid
- Reacts with metal in following manner:
  - a. cold and dilute acid give salt and H_2
  - b. cold and concentrated acid do not react with Cu, Ag, Au, Hg, Pt.
  - c. hot and concentrated acid liberate SO_2 and metallic sulphate
- Good dehydrating agent, removes water from organic compounds and libera CO, CO_2, and black C.
- As an oxidizing agent oxidizes C and S to their oxides, H_2S to S, HBr, HI to B and I_2 respectively.
- Reacts with $BaCl_2$ and $Pb(NO_3)_2$ to give precipitation of $BaSO_4$ and $PbSO_4$
- Reacts with $KMnO_4$ and $K_2Cr_2O_7$ and liberate O_2

GARDEN OF EQUATIONS

NITROUS OXIDE

Preparation

$$4Zn + \underset{\text{dilute}}{10HNO_3} \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

$$NH_4NO_3 \xrightarrow{200°C} N_2O + 2H_2O$$

Chemical Reactions of Nitrous Oxide

$$2N_2O + S \longrightarrow SO_2 + 2N_2$$

$$10N_2O + P_4 \longrightarrow P_4O_{10} + 10N_2$$

$$N_2O + Cu \longrightarrow CuO + N_2$$

NITRIC OXIDE

Preparation

$$3Cu + \underset{\text{dilute}}{8HNO_3} \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$N_2 + O_2 \rightleftharpoons 2NO$$

Chemical Reactions of Nitric Oxide

$NO + O_2 \longrightarrow 2NO_2$

$2NO \longrightarrow N_2 + O_2$

$2NO + Cl_2 \longrightarrow 2NOCl$

$FeSO_4 + NO \longrightarrow FeSO_4 . NO$ (Black ring of nitrosyl ferrous sulphate)

$H_2S + 2NO \longrightarrow H_2O + N_2O + S$

$H_2SO_3 + 2NO \longrightarrow H_2SO_4 + N_2O$

$2HNO_3 + NO \longrightarrow H_2O + 3NO_2$

$H_2O + NO + 3I_2 \longrightarrow 6HI + 2HNO_3$

$6KMnO_4 + 12H_2SO_4 + 10NO \longrightarrow 6KHSO_4 + 4H_2O + 10HNO_3 + 6MnSO_4$

NITROGEN DIOXIDE

Preparation

$\underset{\text{(conc.)}}{Cu + 4HNO_3} \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

$2Pb(NO_3)_2 \longrightarrow 2PbO + 2NO_2 + O_2$

EFFECT OF HEAT

$N_2O_4 \overset{140^\circ C}{\rightleftharpoons} 2NO_2 \overset{620^\circ C}{\rightleftharpoons} NO + O_2$

$2NO_2 \longrightarrow 2NO + O_2$

CHEMICAL REACTION S OF NITROGEN DIOXIDE

$5NO_2 + 2P \longrightarrow P_2O_5 + 5NO$

$H_2O + 2NO_2 \longrightarrow HNO_3 + HNO_2$

$H_2S + NO_2 \longrightarrow H_2O + NO + S$

$2KOH + 2NO_2 \longrightarrow H_2O + KNO_2 + KNO_3$

$2NO_2 + 2KI \longrightarrow I_2 + 2KNO_2$

$2FeSO_4 + H_2SO_4 + NO_2 \longrightarrow Fe_2(SO_4)_3 + H_2O + NO$

$2NaOH + 2NO_2 \longrightarrow H_2O + NaNO_2 + NaNO_3$

NITRIC ACID

Preparation

Birkland and Eyde's process

$N_2 + O_2 \xrightarrow{3000^\circ C} 2NO$

$2NO + O_2 \xrightarrow{600\text{-}1000C} 2NO_2$

$H_2O + 2NO_2 \longrightarrow HNO_3 + HNO_2$

$3HNO_2 \longrightarrow H_2O + NO + HNO_3$

Chapter 4 Group VA & VIA Elements

Chemical Reactions Of Nitric Acid

REACTION WITH BASE

$$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$$

REACTIONS WITH SALTS

$$Na_2CO_3 + 2HNO_3 \longrightarrow 2NaNO_3 + H_2O + CO_2\uparrow$$

$$NaHCO_3 + HNO_3 \longrightarrow NaNO_3 + H_2O + CO_2\uparrow$$

REACTIONS WITH METALS

$$3Cu + \underset{\text{dilute}}{8HNO_3} \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$Cu + \underset{\text{conc}}{4HNO_3} \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

$$4Zn + \underset{\text{dilute}}{10HNO_3} \longrightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

$$Zn + \underset{\text{conc}}{4HNO_3} \longrightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$$

$$3Pb + \underset{\text{dilute}}{8HNO_3} \longrightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O$$

$$Pb + \underset{\text{conc}}{4HNO_3} \longrightarrow Pb(NO_3)_2 + 2NO_2 + 2H_2O$$

$$Mg + 2HNO_3 \xrightarrow{\text{dilute}} Mg(NO_3)_2 + H_2$$

$$Mn + \underset{\text{Conc.}}{4HNO_3} \xrightarrow{\text{dilute.}} Mn(NO_3)_2 + H_2$$

$$Hg + \underset{\text{(excess)}}{4HNO_3} \longrightarrow Hg(NO_3)_2 + 2NO_2 + 2H_2O$$

$$6Hg + \underset{\text{(excess)}}{8HNO_3} \xrightarrow{\text{dilute}} 3Hg_2(NO_3)_2 + 2NO + 4H_2O$$

$$4Sn + 10HNO_3 \xrightarrow{\text{dilute}} 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

$$Sn + 4HNO_3 \longrightarrow \underset{\text{Meta stannic acid}}{H_2SnO_3} + 4NO_2 + H_2O$$

$$Sb + 5HNO_3 \longrightarrow H_3SbO_4 + 5NO_2 + H_2O$$

REACTIONS WITH NON-METALS

$$S + 6HNO_3 \xrightarrow{\text{dilute}} H_2SO_4 + 6NO_2 + 2H_2O$$

$$As + 5HNO_3 \xrightarrow{\text{conc}} H_3AsO_4 + 5NO_2 + H_2O$$

$$As + 3HNO_3 \xrightarrow{\text{dilute}} H_3AsO_3 + 3NO_2$$

$$P + 5HNO_3 \xrightarrow{\text{Hot / conc.}} H_3PO_4 + H_2O + 5NO_2$$

$$I_2 + 10HNO_3 \xrightarrow{\text{Hot / conc.}} 2HIO_3 + 10NO_2 + 4H_2O$$

$$C + 4HNO_3 \xrightarrow[\text{hot}]{\text{conc}} CO_2 + 4NO_2 + 2H_2O$$

REACTIONS AS AN OXIDIZING AGENT

$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$

$3H_2S + 2HNO_3 \longrightarrow 3S + 2NO + 4H_2O$

$6HI + 2HNO_3 \longrightarrow 4H_2O + 2NO + 3I_2$

$SnCl_2 + 2HCl + 2HNO_3 \longrightarrow SnCl_4 + 2NO_2 + 2H_2O$

AQUA REGIA

$HNO_3 + 3HCl \longrightarrow NOCl + Cl_2 + 2H_2O$

$2NOCl \longrightarrow 2NO + Cl_2$

PHOSPHORUS TRICHLORIDE

Preparation

$3P + 3Cl_2 \longrightarrow 2PCl_3$

$2P + 4SOCl_2 \longrightarrow 2PCl_3 + 2SO_2 + S_2Cl_2$

Chemical Reactions of Phosphorus Trichloride

$PCl_3 + Cl_2 \longrightarrow PCl_5$

$PCl_3 + O_2 \longrightarrow 2POCl_3$

$PCl_3 + H_2O \longrightarrow H_3PO_4 + 3HCl$

PHOSPHORUS PENTACHLORIDE

Preparation

$2P + 5Cl_2 \longrightarrow 2PCl_5$

$PCl_3 + Cl_2 \longrightarrow PCl_5$

Chemical Reactions of Phosphorus Pentachloride

$PCl_5 \longrightarrow PCl_3 + Cl_2$

$PCl_5 + Zn \longrightarrow ZnCl_2 + PCl_3$

$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$

PHOSPHORUS TRIOXIDE

Preparation

$P_4 + 3O_2 \longrightarrow 2P_2O_3$

Chemical Reactions of Phosphorus Trioxide

$P_2O_3 + O_2 \longrightarrow P_2O_5$

$P_2O_3 + 3H_2O \xrightarrow{\text{cold}} 2H_3PO_3$

$P_2O_3 + 6H_2O \xrightarrow{\text{hot}} 2H_3PO_4 + PH_3$

PHOSPHORUS PENTOXIDE

Preparation

$$P_4 + 5O_2 \longrightarrow 2P_2O_5$$

Chemical Reactions of Phosphorus Pentaoxide

$$P_2O_5 + H_2O \longrightarrow 2HPO_3$$
$$P_2O_5 + 3H_2O \xrightarrow{\text{cold}} 2H_3PO_4$$
$$P_2O_5 + 2HNO_3 \xrightarrow{\text{hot}} N_2O_5 + 2HPO_3$$
$$P_2O_5 + C_2H_5OH \longrightarrow C_2H_4 + 2HPO_3$$
$$P_2O_5 + 2CH_3COOH \longrightarrow 2HPO_3 + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O}$$

PHOSPHORUS ACID

Preparation

$$P_2O_3 + 3H_2O \longrightarrow 2H_3PO_3$$
$$PCl_3 + 3H_2O \xrightarrow{\text{cold}} H_3PO_3 + 3HCl$$

Chemical Reactions of Phosphorus Acid

$$4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$$
$$H_3PO_3 + CuSO_4 + H_2O \longrightarrow H_3PO_4 + H_2SO_4 + Cu$$
$$H_3PO_3 + 2AgNO_3 + 2NH_4OH \longrightarrow H_3PO_4 + H_2O + 2Ag + 2NH_4NO_3$$
$$H_3PO_3 + O_2 \longrightarrow 2H_3PO_4.$$
$$H_3PO_3 + 6[H] \xrightarrow{Zn/HCl} PH_3 + 3H_2O$$

ORRTHOPHOSPHORIC ACID

Preparation

$$P_2O_5 + 3H_2O \xrightarrow{\text{hot}} 2H_3PO_4$$
$$P + 5HNO_3 \longrightarrow H_3PO_4 + 5NO_2 + H_2O$$
$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$
$$Ca_3(PO_4)_2 + 3SiO_2 \longrightarrow 3CaSiO_3 + P_2O_5$$

Chemical Reactions of Orthophosphoric Acid

DEHYDRATION

$$2H_3PO_4 \xrightarrow[-H_2O]{240^\circ C} H_4P_2O_7 \xrightarrow[-H_2O]{316^\circ C} 2HPO_3$$

REACTION WITH BASE

$H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$

$H_3PO_4 + 2NaOH \longrightarrow Na_2HPO_4 + H_2O$

$H_3PO_4 + 3NaOH \longrightarrow Na_3PO_4 + H_2O$

SULPHURIC ACID

Preparation

Contact Process

$S + O_2 \longrightarrow SO_2$

$2SO_2 + O_2 \xrightarrow[V_2O_5,]{400\text{-}500^\circ C} 2SO_3$

$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7$

$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$

Chemical Reactions of Sulphuric Acid

IONIZATION

$H_2SO_4 + H_2O \longrightarrow H_3O^+ + HSO_4^-$

$HSO_4^- + 2H_2O \longrightarrow 2H_3O^+ + SO_4^{-2}$

REACTIONS WITH BASE

(A) Arrhenius Base

$H_2SO_4 + NaOH \longrightarrow NaHSO_4 + H_2O$

Sodium bisulphate
(acidic salt)

$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O$

Sodium sulphate
(normal salt)

(B) Lewis Base

$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$

REACTIONS WITH METALS

(A) Cold and dilute sulphuric acid

$Mg + H_2SO_4 \longrightarrow MgSO_4 + H_2$

$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$

$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$

$Sn + H_2SO_4 \longrightarrow SnSO_4 + H_2$

(B) Hot and concentrated sulphuric acid

$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$

$2Ag + 2H_2SO_4 \longrightarrow Ag_2SO_4 + SO_2 + 2H_2O$

$Hg + 2H_2SO_4 \longrightarrow HgSO_4 + SO_2 + 2H_2O$

REACTIONS WITH SALTS

$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + CO_2 + H_2O$

$CuCO_3 + H_2SO_4 \longrightarrow CuSO_4 + CO_2 + H_2O$

$2NaHCO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2CO_2 + 2H_2O$

$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$

$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$

REACTIONS AS AN OXIDIZING AGENTS

$H_2S + H_2SO_4 \longrightarrow S + SO_2 + 2H_2O$

$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$

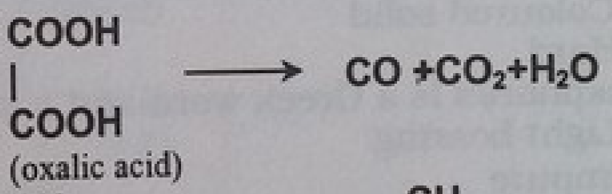
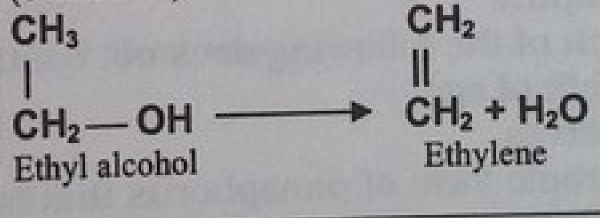
$C + 2H_2SO_4 \longrightarrow CO_2 + 2SO_2 + 2H_2O$

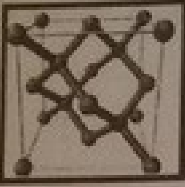
$2P + 4H_2SO_4 \longrightarrow H_3PO_3 + H_3PO_4 + 4SO_2 + H_2O$

$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$

REACTIONS AS A DEHYDRATING AGENT

Concentrated sulphuric acid

$C_6H_{12}O_6 \longrightarrow 6C + 6H_2O$ (glucose)	 $\begin{array}{c}COOH\\ \vert \\ COOH\end{array} \longrightarrow CO + CO_2 + H_2O$ (oxalic acid)
$C_{12}H_{22}O_{11} \longrightarrow 12C + 11H_2O$ (Sucrose)	 $\begin{array}{c}CH_3\\ \vert \\ CH_2—OH\end{array} \longrightarrow \begin{array}{c}CH_2\\ \Vert \\ CH_2\end{array} + H_2O$ Ethyl alcohol → Ethylene
$HCOOH \longrightarrow CO + H_2O$ (Formic acid)	



PRACTICE EXERCISE

20 min Time Yourself

1. Which of the following is different with respect to physical appearance?
   (a) Arsenic
   (b) Phosphorus
   (c) Antimony
   (d) Bismuth
2. Which one of the followings possesses melting point below 0°C?
   (a) Nitrogen
   (b) Phosphorus
   (c) Carbon
   (d) Bismuth
3. Compounds of nitrogen and phosphorus are mostly
   (a) ionic
   (b) covalent
   (c) polar
   (d) all varieties are possible
4. The most electronegative element among the following is
   (a) Sb
   (b) N
   (c) As
   (d) P
5. SO_3 is not absorbed in water directly because
   (a) Reaction is exothermic
   (b) It is insoluble in water
   (c) Dilute acid is produced
   (d) All of above
6. Phosphene gas will be produced if phosphorous acid is subjected to
   (a) Oxidation
   (b) Reduction
   (c) Decomposition
   (d) Both b & c
7. Which of the following will give phosphoric acid on reaction with water
   (a) PCl_5
   (b) P_2O_3
   (c) P_2O_5
   (d) All of the above
8. Which one of following is not a property of pure quartz?
   (a) Coloured solid
   (b) Brittle
   (c) Hard
   (d) All of above
9. Phosphorus is a Greek word and it means
   (a) Light bearing
   (b) Fire
   (c) Impure
   (d) Tetrahedral
10. Which of the following does not contain phosphorus?
    (a) Yolk of egg
    (b) Bone
    (c) Nerves
    (d) Steel
11. Allotropic form of phosphorus that is poisonous is
    (a) White
    (b) Red
    (c) Black
    (d) Violet
12. Which one of the following is not the use of graphite?
    (a) Lead pencils
    (b) Abrasive
    (c) Lubricant
    (d) Electrode of electrolytic cell
13. Acetic anhydride can be obtained by treating ethyl alcohol with
    (a) P_2O_5
    (b) H_2SO_4
    (c) Both a & b
    (d) PCl_5
14. The composition of brown ring in nitrate test is
    (a) $FeSO_4.NO$
    (b) $FeSO_4.NO_2$
    (c) $FeSO_4.NO_3$
    (d) $FeSO_4.N_2O$
15. Phosphorous acid upon thermal decomposition yields phosphoric acid and
    (a) Phosphine
    (b) Phosphorus
    (c) Water
    (d) Phosphorus pentoxide

16. Which one of the following compounds usually smells like garlic?
(a) P_2O_3
(b) P_2O_5
(c) H_3PO_3
(d) All have same smell

17. P_2O_5 is a hygroscopic powder which sublimes at
(a) 260°C
(b) 360°C
(c) 630°C
(d) 620°C

18. The element of group VIA, which is a non-metal is
(a) S
(b) Se
(c) Te
(d) Po

19. Phosphoric acid is a weak acid and its basicity is
(a) 1
(b) 3
(c) zero
(d) 2

20. All the elements in group VIA are ________ in nature.
(a) hygroscopic
(b) metals
(c) polymeric
(d) all of above

21. Which of the elements show passivity when treated with conc. HNO_3.
(a) Fe
(b) Aℓ
(c) Cr
(d) All of the above

22. Which allotropic form of phosphorous is the most stable?
(a) white
(b) black
(c) red
(d) Violet

23. The gas which cannot be dried by conc. H_2SO_4
(a) SO_2
(b) H_2S
(c) CO_2
(d) C_2H_4

24. The chemical composition of cinnabar is
(a) ZnS
(b) PbS
(c) HgS
(d) FeS

25. $FeSO_4$ forms brown ring with
(a) N_2O_3
(b) NO_2
(c) NO
(d) N_2O

26. Oxygen and sulphur resemble in all except
(a) Electronic configuration of valence shell electrons.
(b) Show allotropy
(c) Polymeric
(d) Show same oxidation state

27. Oxygen does not react with all except
(a) Alkali
(b) Acid
(c) Water
(d) Metals

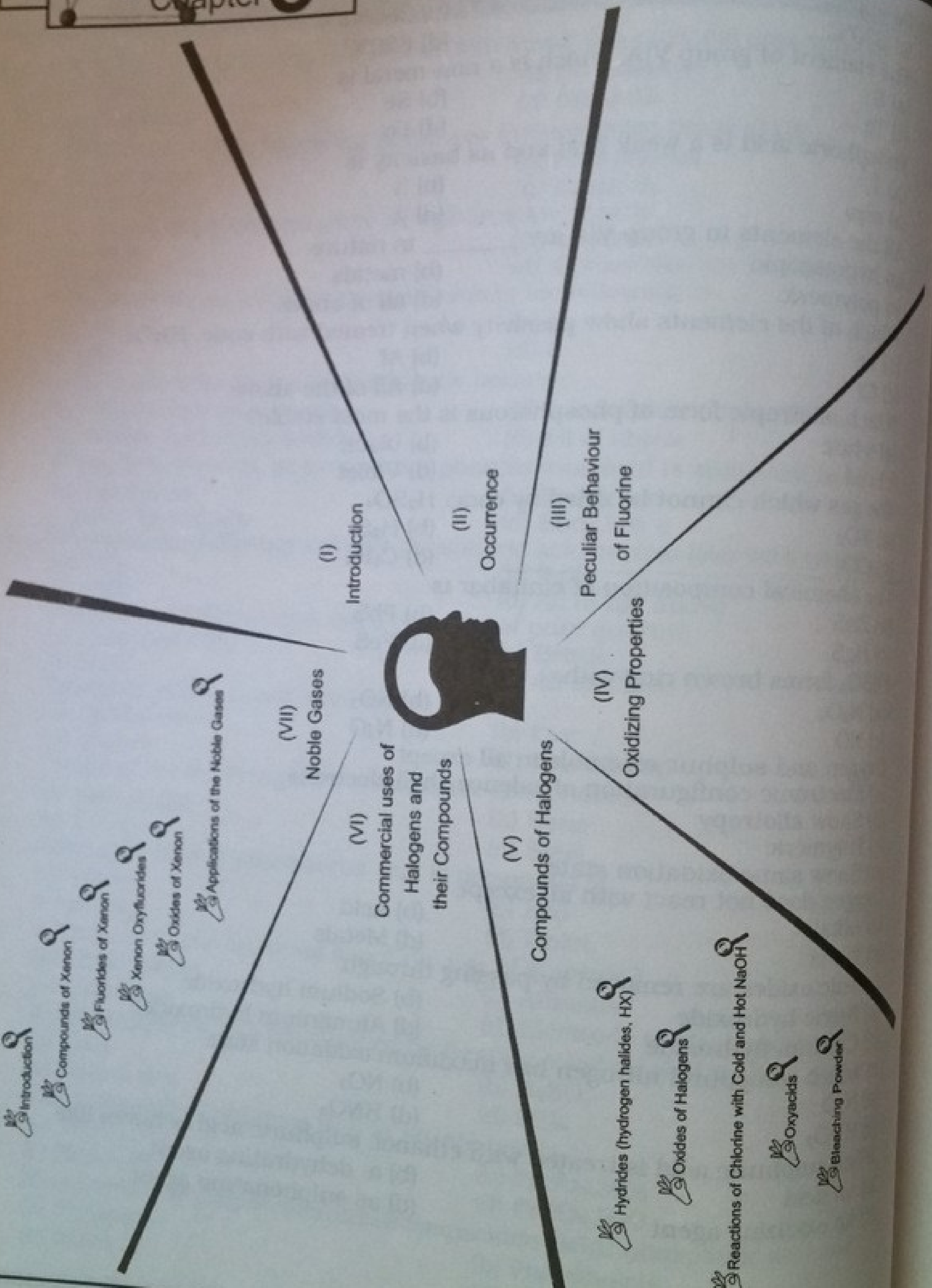
28. Arsenic oxides are removed by passing through
(a) Ferric hydroxide
(b) Sodium hydroxide
(c) Calcium hydroxide
(d) Aluminium hydroxide

29. In which compound nitrogen has maximum oxidation state
(a) N_2O
(b) NO_2
(c) HNO_2
(d) HNO_3

30. When sulphuric acid is treated with ethanol, sulphuric acid behaves like
(a) an acid
(b) a dehydrating agent
(c) an oxidizing agent
(d) as sulphonating agent

Chapter 5

THE HALOGENS & THE NOBLE GASES



INTRODUCTION (HALOGENS)

- VII-A group is called halogen group.
- Very reactive with non-metals.
- Exist in three states of matter with diatomic molecule.
- Halogen forms –ve ion by getting one electron (X^-).
- Have highest E.N. value among the elements of their period.

Astatine is rare element. It is a radioactive and its most stable isotope has half-life of 8.30 hrs.

	FLUORINE	CHLORINE	BROMINE	IODINE
Colour	Pale yellow	Greenish yellow	Reddish brown	metallic shiny Greyish black
Physical state	Gas	Gas	Liquid	Solid

OCCURRENCE OF HALOGENS

- Halogens are very reactive, so they are not found in free state.
- Halogens are found in the form of soluble halides.

FLUORINE	CHLORINE	BROMINE	IODINE
Fluorospar CaF_2 Cryolite Na_3AlF_6 Apatite [$CaF_3.3Ca_3(PO_4)_2$]	Halite NaCl (Salt beds, brine wells, sea water) Carnalite $KCl.MgCl_2.6H_2O$	Brine wells, Sea water NaBr, KBr, $MgBr_2$	$NaIO_3$, $NaIO_4$ deposits in Chile brine wells

PECULIAR BEHAVIOUR OF FLOURINE

Fluorine	Other Halogen
High first I.P and E.N	Low first I.P and E.N
Low dissociation energy	High dissociation energy except I_2
Fluorides have high lattice energy .	Lattice energy of other halides is smaller than other fluorides
Most reactive	Less reactive
F reacts directly with noble gases	No other halogen reacts with the noble gases
Shows only -1 oxidation state	Others show -1,+1,+3,+5,+7 oxidation states
Does not form oxy acids.	Form oxiacids.
Has maximum reduction potential.	Others have lower reduction potential.

OXIDIZING PROPERTIES OF HALOGENS

- The oxidizing power of halogens decreases with increase in atomic number. $F_2 > Cl_2 > Br_2 > I_2$
- The oxidizing power of halogens depend upon the following factors:
  - Energy of dissociation.
  - Electron affinity of atoms
  - Hydration energies of ions.
  - Heats of vaporization (for Br_2 and I_2)
- Fluorine and chlorine can oxidize various coloured dyes to colourless substances e.g. litmus and universal indicator can be decolourized when exposed to fluorine or chlorine.

COMPOUNDS OF HALOGEN

HYDRIDES

The binary compounds of X and H are hydrides.

- Reactivity of X_2 with H_2 is $F > Cl > Br > I$.
- Reaction with I_2 is reversible and very slow.
- F and Cl give their halides with conc. H_2SO_4 while Br and I do not.

Properties Of Hydrides

Properties of HF

- Zig-Zag pattern of hydrogen bonding is present in HF.
- HF is liquid while HCl, HBr and HI are gases at room temperature.
- HF attacks glass while others do not.
- Viscosity of HF is lesser than water.
- Vapour phase of HF is equilibrium mixture of monomers and cyclic hexamers.

Properties Of other Hydrogen Halide

Increasing Trends

- Intermolecular attraction, M.P, B.P, heat of fusion, heat of vaporization, bond length, reducing strength and acidic strength is in the order as
  $HCl < HBr < HI$

Decreasing Trends

- Bond energy, Dipole moment, Strength of bond have trends as $HCl > HBr > HI$

OXIDES OF HALOGENS

- No reaction with Oxygen under normal conditions except fluorine.

Fluorine	Chorine	Bromine	Iodine
Oxygen diflouride OF_2	Dichlorine monoxide Cl_2O	Bromine monoxide Br_2O	Iodine tetraoxide I_2O_4
Dioxygen diflouride O_2F_2	Chlorinedioxide ClO_2	Bromine dioxide BrO_2	Iodine iodate I_4O_9
Trioxygen diflouride O_3F_2	Chlorine hexaoxide Cl_2O_6	Bromine trioxide BrO_3 (Br_3O_8)	Iodine pentaoxide I_2O_5
	Chlorine heptaoxide Cl_2O_7		

	Preparation	Colour and state	Effect of heat	Uses and other properties
O_3F_2	From mixture of F_2 and O_2 subjected to electric discharge	▪ Dark red liquid at 363°C ▪ Reddish brown solid at 350°C	Gives oxygen and oxides of flourine	On reaction with F_2, it gives O_2F_2
ClO_2	▪ By reducing $NaClO_3$ with NaCl or SO_2 or CH_3OH in acidic media ▪ By reacting H_2SO_4 and $KClO_3$ in the presence of oxalic acid	Pale yellow gas	Forms O_2 and Cl_2 on warming	▪ Paramagnetic substance ▪ Used as antiseptic for purification of water and bleach of cellulose material ▪ Decomposes in H_2O to HCl and $HClO_3$
Cl_2O_7	By dehydration of perchloric acid ($HClO_4$) with P_2O_5 at -10°C	Colourless viscous liquid	Stable at room temperature	When goes in water produces $HClO_4$.
Br_2O	By reacting bromine vapours and mercuric oxide By suspension of mercuric oxide in CCl_4 and Br_2	Dark Volatile liquid	Only stable at -20°C	It has oxidizing properties
I_2O_5	Heating iodic acid at 240°C	White crystalline solid	Stable up to 300°C	▪ Has polymeric structure ▪ Insoluble in organic solvent ▪ Acts as oxidizing agent ▪ Used in quantitative analysis of CO

DISPROPORTIONATION REACTION

A reaction in which a specie is simultaneously oxidized and reduced is called disproportionation reaction.

e.g. reaction of Cl_2 with NaOH gives sodium hypochlorite and sodium chloride.

In this reaction, oxidation of chlorine converts it into chloride (-1) and hypochlorite (+1) in cold state. At 70°C the oxidation state changes from -1 to +5.

OXYACIDS

- In oxyacids, X is the central atom to which one or more oxygen atoms are covalently bonded.
- Greater number of O atom in oxyacids, more will be thermal stability.
- Acidic strength increases with increase in oxygen atom
- Strength of oxyacids is $HXO_4 > HXO_3 > HXO_2 > HXO$.

- Chloric acid is stroger than bromic acid. It is due to decrease in electronegativity and increase in the size of bromine.

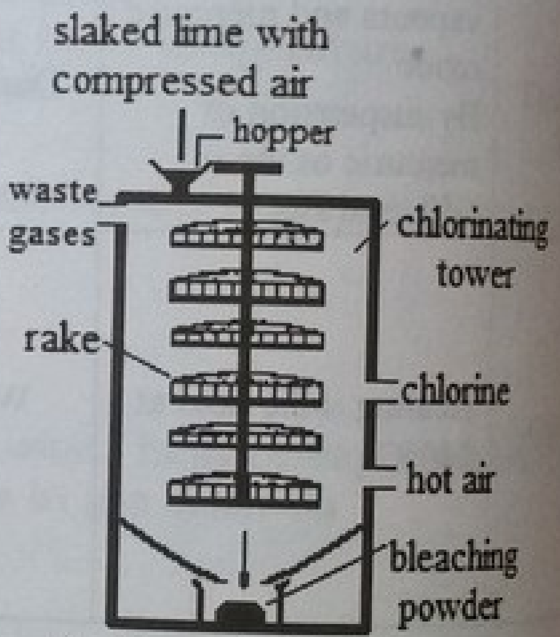
Oxidation state of halogen	Formula of oxcyacids of halogens			General names of	
	Chlorine	Bromine	Iodine	Oxyacids	Salts of oxyacids
+1	$HClO$	$HBrO$	HIO	Hypohalous acid	Hypo------ite
+3	$HClO_2$	--------------	--------------	Halous acid	------------ite
+5	$HClO_3$	$HBrO_3$	HIO_3	Halic acid	------------ate
+7	$HClO_4$		HIO_4,H_5IO_6	Perhalic acid	Per--------ate

PERCHLORIC ACID

- It is prepared by distilling a mixture of potassium perchlorate and conc. H_2SO_4 under reduced pressure.
- Perchloric acid is a hygroscopic liquid.
- Freezes at -112°C, decomposes at 90°C
- It works as oxidizing agent.
- It is stored in 67% solution in water as decomposes explosively when heated
- Due to its oxidizing property, it is very important analytical reagent.

BLEACHING POWDER

- It is prepared by reaction of slaked lime and chlorine
- Two methods are available
  - Hasenclever method (old)
  - Beckman method (new)
- It is good oxidizing agent due to generation of hypochorite ion.
- Cl_2 is liberated on reaction with excess acid Cl_2 is called "available chlorine" (35-40%).



Beckmann's Method

- **Uses**
  - Preparation of chloroform
  - Sterilization of water
  - Preparation of un-shrinkable wool
  - As bleaching agent in textile

COMMERCIAL USE OF HALOGENS AND COMPOUNDS

Field of usage	Fluorine	Chlorine	Bromine	Iodine
Chemical	▪ Freon gas CCl_2F_2, $CClF_3$, CF_4 ▪ Teflon (valuable plastic) $(-CF_2-CF_2-)$	▪ Bleaching powder ▪ PVC ▪ CCl_4 ▪ $CHCl_3$ ▪ HCl	▪ Ethylene bromide $C_2H_4Br_2$ used in gasoline to save engine PbO and deposits $PbSO_4$	▪ KI, NaI are added to common salt which is known as iodized salt.
Industry	▪ Corrosion proof parts of machinery from Teflon ▪ Electric wires are coated with Teflon	▪ Bleaching powder is used in textile and paper industry.	▪ AgBr is used in photography.	▪ Pharmaceutical industry as disinfectant and germicide.
Medical /agriculture	▪ Halothane is used as anesthetic	▪ Antiseptic, insecticide weed killer, herbicide	▪ Used as fungicide	▪ To fulfill deficiency of I_2 in our diet to avoid the risk of goiter

INTRODUCTION (NOBLE / RARE GASES)

- Noble gases are placed in zero group or VIII-A group
- All elements are non-metallic, odourless & colourless gases.
- There are eight electrons in outermost shell of each element except He.
- Noble gases are isolated from air by fractional distillation.
- He is present on earth as radioactive decay, the 2nd most abundant element in the universe.
- Neon is 1/65000th part of air.
- Neon gives reddish glow in gas discharge tube.
- Neon has 40 times more refrigeration capacity than He.
- Xe is present in air as 0.08 ppm.
- Radon is product as α-decay of radium.
- Boiling point increases down the group due to increase in London forces.

COMPOUNDS OF Xe

Oxidation state of Xe	Compound	Physical state
+2	XeF_2	Colourless crystal
+4	XeF_4, $XeOF_2$	Colourless crystal
+6	XeF_6	Colourless crystal
	$XeOF_4$	Colourless liquid
	XeO_3	Colourless crystal
+8	XeO_4	Colourless gas

FLOURIDES

Particulars	XeF_2	XeF_4	XeF_6
Preparation	Direct interaction of Xe and F_2 for 8 hours	Interaction of Xe and F_2 in 1:5 ratio in Nickel container at 6 atm for few hours	Interaction of Xe and F_2 in 3:20 ratio in stainless steel vessel at 50 atm and 300°C
State	Crystalline solid	Crystalline solid	Crystalline solid
Others	▪ Stored in Ni vessel ▪ Mild fluorinating agent	▪ Stored in Ni vessel ▪ Strong fluorinating agent	Yellow in colour when liquid or gas
Action of H_2	Forms Xe and HF	Forms Xe and HF	Forms Xe and HF
Hydrolysis	HF, O_2, Xe	XeO_3, HF, O_2, Xe	Forms HF and $XeOF_4$
Action of NH_3	-	Forms N_2, HF & Xe	-
Action of Hg	-	Forms Xe and HgF_2	-

XENON OXYTETRAFLUORIDE ($XeOF_4$)

- Prepared by XeF_6 and quartz (silica).
- Colourless volatile liquid
- Stored in Ni vessel
- Gives XeO_3 after reaction with water

XENON OXIDES

Particulars	XeO_3	XeO_4
Preparation	Interaction of XeF_6 and H_2O	Interaction of Ba_2XeO_6 or Na_4XeO_6 with H_2SO_4
State and other	▪ Crystalline solid ▪ Explodes at very low temp. ▪ Weak acid	Yellow crystalline solid below -35.9°C

USES OF NOBLE GASES

- He ⇒ weathering balloons, traffic signal lights and welding
- 80%He + 20%oxygen ⇒ breathing cylinder
- He ⇒ cooling in nuclear reactor
- Ne ⇒ neon advertising signs, TV tubes, high voltage indicators
- Ne+He ⇒ making glass lasers
- Ar ⇒ bulbs, fluorescent tubes, radio tubes
- Ar ⇒ arc welding
- Kr ⇒ filled in fluorescent tube, flash lambs
- Xe ⇒ bactericidal lamps
- Ra ⇒ radiotherapy of cancer, earthquake prediction

GARDEN OF EQUATIONS

OXIDES OF HALOGENS

$$2O_3F_2 \longrightarrow 2O_2F_3 + O_2$$

$$2O_3F_2 + F_2 \longrightarrow 3O_2F_2$$

$$5CO + I_2O_5 \longrightarrow I_2 + 5CO_2$$

OXYACIDS OF HALOGENS

$$2HClO_4 + P_2O_5 \xrightarrow{-10^\circ C} Cl_2O_7 + 2HPO_3$$

$$HgO + 2Br_2 \xrightarrow{50^\circ C} HgBr_2 + Br_2O$$

$$2HIO_3 \xrightarrow{240^\circ C} I_2O_5 + H_2O$$

DISPROPORTIONATION REACTIONS

$$\begin{array}{rcl} [Cl_2 + 2NaOH & \xrightarrow{15^\circ C} & NaCl + NaClO + H_2O] \times 3 \\ 3NaClO & \longrightarrow & 2NaCl + NaClO_3 \\ \hline 3Cl_2 + 6NaOH & \xrightarrow{70^\circ C} & NaClO_3 + 5NaCl + 3H_2O \end{array}$$

BLEACHING POWDER

IONIZATION

$$Ca(OCl)\,Cl \overset{H_2O}{\rightleftharpoons} Ca^{2+} + Cl^- + ClO^-$$

REACTION WITH LEWIS BASE

$$3Ca(OCl)Cl + 2NH_3 \longrightarrow 3CaCl_2 + N_2 + 3H_2O$$

REACTION WITH ARHENIUS ACID

$$3Ca(OCl)Cl + 2HCl \longrightarrow CaCl_2 + Cl_2 + H_2O$$

$$2Ca\,(OCl)\,Cl + dil.H_2SO_4 \longrightarrow CaSO_4 + CaCl_2 + 2HClO$$

$$Ca\,(OCl)\,Cl + \underset{(Excess)}{H_2SO_4} \longrightarrow CaSO_4 + H_2O + Cl_2$$

FLOURIDES OF XENON

Preparation

$$Xe + F_2 \longrightarrow XeF_2$$

$$XeF_2 + F_2 \longrightarrow XeF_4$$

$$XeF_4 + F_2 \longrightarrow XeF_6$$

Chemical Reactions of Xenon Fluorides

AS FLOURINATING AGENTS

$XeF_2 + H_2 \longrightarrow Xe + 2HF$

$XeF_4 + 2H_2 \longrightarrow Xe + 4HF$

$XeF_6 + 3H_2 \longrightarrow Xe + 6HF$

$XeF_4 + 2Hg \longrightarrow Xe + 2HgF_2$

$XeF_4 + 4NH_3 \longrightarrow 3Xe + 12HF + 2N_2$

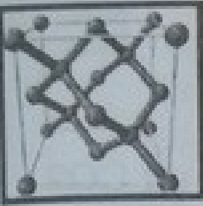
$2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$

$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$

PREPARATION OF XENON OXIDE

$Ba_2XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2BaSO_4 + 2H_2O$

$Na_4XeO_6 + 2H_2SO_4 \longrightarrow XeO_4 + 2Na_2SO_4 + 2H_2O$



PRACTICE EXERCISE

20 mins Time Yourself

1. Among the halogens, the rare element is
(a) Fluorine
(b) Chlorine
(c) Astatine
(d) Iodine

2. The colour of chlorine gas is
(a) pale yellow
(b) greenish yellow
(c) reddish brown
(d) grayish black

3. Vander Waal's forces are stronger in
(a) F_2
(b) Cl_2
(c) Br_2
(d) I_2

4. The most powerful oxidizing agent among the halogens is
(a) F_2
(b) Cl_2
(c) Br_2
(d) I_2

5. Which of the following statements is incorrect about fluorine
(a) fluorine is restricted to -1 oxidation state
(b) fluorine follows octet rule and as well as extended octet rule
(c) fluorine has lowest dissociation energy among the halogens
(d) both b & c

6. The halogen which reacts spontaneously with gold(Au) to form Au^{+3} is
(a) F_2
(b) Cl_2
(c) Br_2
(d) I_2

7. Which one of the following is the weakest acid in water
(a) HF
(b) HCl
(c) HBr
(d) HI

8. The halogen, which reacts very slowly with halogen is
(a) Fluorine
(b) Chlorine
(c) Bromine
(d) Iodine

9. Which of the following represents the correct electronic configuration of VII A group elements in the ground state?
(a) ns^2p^2
(b) ns^2p^4
(c) ns^2p^5
(d) ns^2p^6

10. The halogen having highest electron affinity is
(a) Fluorine
(b) Chlorine
(c) Bromine
(d) Iodine

11. Which is the strongest acid?
(a) HClO
(b) $HClO_2$
(c) $HClO_3$
(d) $HClO_4$

12. Bromine can be liberated from KBr solution by the action of
(a) Iodine solution
(b) Chlorine
(c) NaCl
(d) KI

13. Bleaching powder is an example of
(a) Normal salt
(b) Double salt
(c) Mixed salt
(d) Complex

14. Consider the following reaction-
$2KClO_3 + H_2C_2O_4 + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O + 2CO_2 + \text{Oxide}$
Which oxide of chlorine is produced in the above reaction?
(a) Cl_2O
(b) ClO_2
(c) Cl_2O_6
(d) Cl_2O_7

15. Which of the following oxides of iodine is used for quantitative analysis of CO?
(a) I_2O_4
(b) I_4O_2
(c) I_2O_5
(d) All are equally useful

16. Consider the following reaction-
$3Cl_2 + 6NaOH \longrightarrow NaClO_3 + 5NaCl + 3H_2O$
This reaction is
(a) Displacement reaction
(b) Double displacement reaction
(c) Disproportionation reaction
(d) Reduction reaction

17. Which of the halogen has highest electronegativity?
(a) Fluorine
(b) Chlorine
(c) Bromine
(d) Iodine

18. Which of the halogen can displace other three elements?
(a) Fluorine
(b) Chlorine
(c) Iodine
(d) Bromine

19. Which of the following statements is incorrect about halogens?
(a) All are non-metals
(b) All the halogens have electronic configuration ns^2p^5
(c) They have high electron affinity and ionization energy
(d) All the halogens react with noble gases to form their halides

20. The chemical formula of sodium hypochlorite is
(a) $NaClO$
(b) $NaClO_2$
(c) $NaClO_3$
(d) $NaClO_4$

21. Fluorine can react with
(a) Xe
(b) Kr
(c) Rn
(d) All of the above

22. Bleaching powder is not used for bleaching
(a) Cotton
(b) Costly fabrics
(c) Linen
(d) Paper pulb

23. Which of the following is the weakest reducing agent.
(a) HF
(b) HBr
(c) $HC\ell$
(d) HI

24. Which of the following is not use of compounds of Fluorine
(a) SbF_3 is used for manufacture of pottery
(b) Sodium fluoroacetate is a rat poison
(c) Cu F_2 is used in ceramic industry
(d) None of the above.

25. In which compound of Xenon, the oxidation state of Xenon is + 6.
(a) XeF_4
(b) $XeOF_4$
(c) $XeOF_2$
(d) Na_4XeO_6

26. Photographic plates are coated with a thin film of:
(a) $AgNO_3$
(b) AgI
(c) AgCl
(d) AgBr

27. The anhydride of $HClO_4$ is:
(a) Cl_2O (b) Cl_2O_6
(c) ClO_2 (d) Cl_2O_7

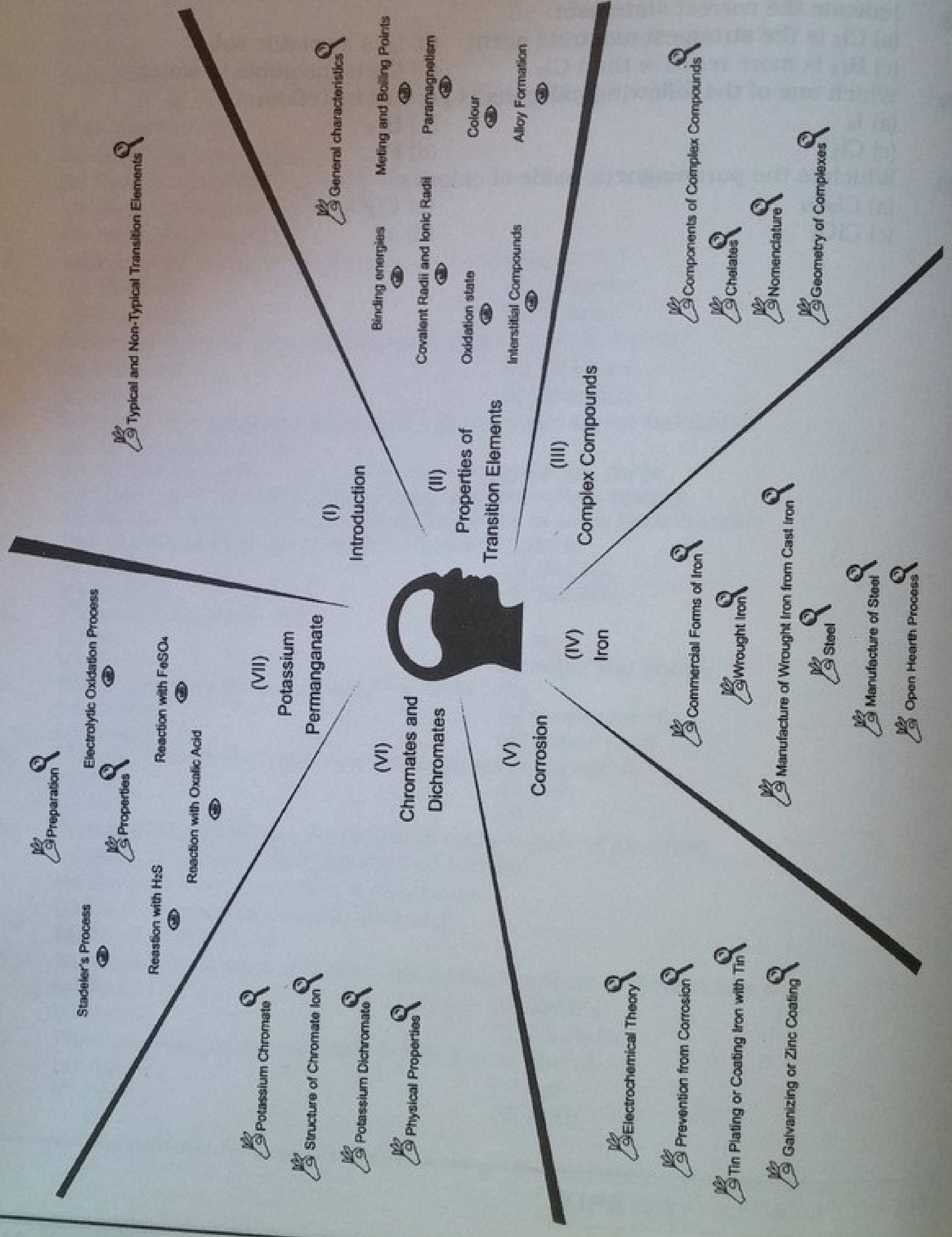
28. Indicate the correct statement:
(a) Cl_2 is the strongest oxidizing agent (b) I_2 is a volatile solid
(c) Br_2 is more reactive than Cl_2 (d) Cl_2 is insoluble in water

29. Which one of the following halogens is present in Teflon:
(a) I_2 (b) Br_2
(c) Cl_2 (d) F_2

30. Which is the paramagnetic oxide of chlorine:
(a) Cl_2O_7 (b) Cl_2O_6
(c) ClO_2 (d) all

Chapter 6

TRANSITION ELEMENTS



Chapter 6

Transition Elements

INTRODUCTION

Transition elements may be defined as those elements which have partially filled 'd' or 'f-sub shells in atomic state or in any of their commonly occurring oxidation states.

Properties

Transition elements usually show variable oxidation states, colour compound and form complex compounds

3d – series elements			
Elements	Electronic Configuration	3d	4s
Sc (21)	[Ar] $3d^1 4s^2$	↑	↑↓
Ti (22)	[Ar] $3d^2 4s^2$	↑ ↑	↑↓
V (23)	[Ar] $3d^3 4s^2$	↑ ↑ ↑	↑↓
Cr (24)	[Ar] $3d^5 4s^1$	↑ ↑ ↑ ↑ ↑	↑
Mn (25)	[Ar] $3d^5 4s^2$	↑ ↑ ↑ ↑ ↑	↑↓
Fe (26)	[Ar] $3d^6 4s^2$	↑↓ ↑ ↑ ↑ ↑	↑↓
Co (27)	[Ar] $3d^7 4s^2$	↑↓ ↑↓ ↑ ↑ ↑	↑↓
Ni (28)	[Ar] $3d^8 4s^2$	↑↓ ↑↓ ↑↓ ↑ ↑	↑↓
Cu (29)	[Ar] $3d^{10} 4s^1$	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑
Zn (30)	[Ar] $3d^{10} 4s^2$	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓

Typical and Non-Typical Transition Elements

- Elements of group II-B(Zn, Cd and Hg), III-B(Sc,Y, La) are non-typical transition elements.
- Coinage metals (Ag,Au and Cu) are considered as transition elements as their d-orbitals are in process of completion in their ionic states.
-
  - ➢ Cu^{+2} ------------ $3d^9$
  - ➢ Ag^{+2} ------------ $4d^9$
  - ➢ Au^{+3} ------------ $5d^8$
- f-block elements are called inner transition elements while d-block elements are called outer transition elements.

GENERAL CHARACTERISTICS OF TRANSITION ELEMENTS

Characteristic	Description
Binding energies	▪ Metals are hard having high value of binding energy due to the involvement of electrons of d-atomic orbitals along with s-atomic orbitals ▪ From Left to Right in a period, the number of unpaired electrons increases up to VI-B and then there is a decrease up to the end of the period. ▪ Binding energy increases up to VI-B and than weakened up to II-B

Melting point and Boiling point	▪ High M.P and B.P due to high binding energy up to 'Vanadium' ▪ And decreases by the end of series
Covalent and ionic radii	▪ Covalent radii decreases rapidly in the start (Sc to V) constant in middle (V to Co) and then begin to increase at the end of series (Ni to Zn) ▪ Ionic radii remain irregular throughout series
Para magnetism	▪ Weakly attracted by strong magnetic field hence are paramagnetic ▪ Unpaired electron favours paramagnetism.
Oxidation state	▪ Elements shows variable oxidation state +2,+3……+7 ▪ It is due to the involvement of unpaired electrons of d with s atomic orbital in bond formation ▪ Sc upto Mn oxidation states increases and after that it decreases
Colour	▪ When d-orbitals are involved in the bonding they split up into two energy levels. One set has a higher energy than the other. ▪ d-d transition occur when light energy absorbs by electrons of lower atomic orbital. ▪ Electron transmits the remaining set of wave length giving colour ▪ Energy difference of d-orbitals varies from ion to ion
Interstitial compounds	▪ The interatomic spaces among metal atoms called interstices ▪ C,B, N, H enters to interstices and form compounds. ▪ They are non-stoichiometric compounds
Alloy formation	▪ Owing to the similarity in their sizes, some transition elements form metallic lattice. ▪ In alloy sheets,Fe is replaced by Cr, Mn, Ni ▪ Examples include brass, bronze etc.

COMPLEX COMPOUNDS

The compounds containing the complex molecules or complex ions and capable of independent existence are called coordination compounds complexes.

A complex compound may contain

(i) A simple cation and a complex anion

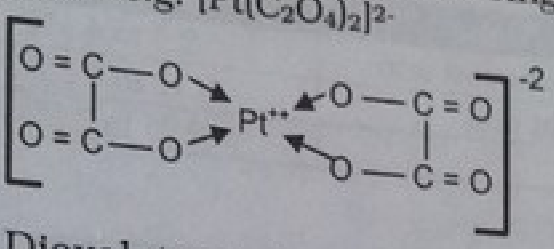
(ii) A complex cation and a simple anion

COMPONENT OF COMPLEX COMPOUND

Component	Description
Central metal atom or ion	▪ Metal atom or metal ion is surrounded by species in the complex compound
Ligand	▪ Ion, atom or neutral molecule that donates electrons to central metal atom/ion. ▪ Ligand with two donor atoms is called bidentate
Co-ordination Number.	▪ The number of lone pair of electrons provided by ligands to central atom or ion.
Co-ordination sphere	▪ The central metal atom or ion along with ligands is called ▪ co-ordination sphere
Charge on co-ordination sphere	▪ Algebraic sum of charges of central metal ion and the total charge on the of ligands

Chelates:

A complex compound, in which one or more than one ring is formed due to donation of electrons by poly dentate ligand. e.g. $[Pt(C_2O_4)_2]^{2-}$



Dioxalato-platinate (II) ion or $[Pt(C_2O_4)_2]^{-2}$

Nomenclature

The IUPAC rules for naming the complex compounds are as follows.

(1) Cations are named before anions.

(2) In naming the coordination sphere, ligands are named in alphabetical order regardless of the nature and number of each followed by the name of central metal ion.

(3) The prefixes di, tri, tetra, penta, hexa, etc, are used to specify the number of coordinated same ligand.

(4) The names of anionic ligands end in suffix "O" e.g. hydroxo, OH^- carbonato $CO_3{}^{2-}$.

(5) The names of neutral ligands are usually unchanged, e.g. for NH_3 ammine and for H_2O, aqua......etc.

(6) The suffix 'ate' comes at the end of the name of metal if the complex represents an anion, otherwise it remains unchanged.

(7) The oxidation number of the metal ion is represented by a Roman numeral in parenthesis following the name of the metal.

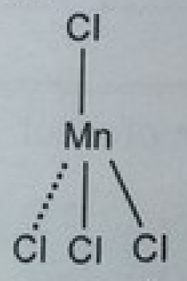
Examples:

$K_4[Fe(CN)_6]$ Potassium hexacayno ferrate(II)

$[PtCl(NO_2)(NH_3)_4]SO_4$ Tetraammine chloronitro-platinum (IV) sulphate.

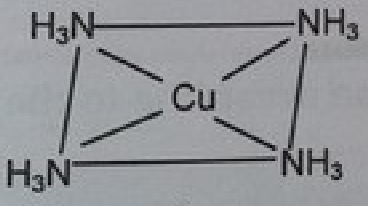
Geometry Of Complex Compound

$[MnCl_4]^{-2}$



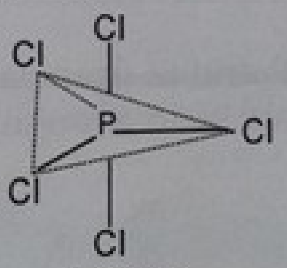
tetrahedral (sp^3)

$[Cu(NH_3)_4]^{+2}$



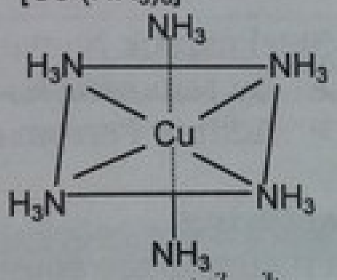
square planar (dsp^2)

$[PCl_5]$



trigonal bipyramidal (dsp^3)

$[Co(NH_3)_6]^{+3}$



octahedral (d^2sp^3)

IRON

Ores of iron

Name	Formula
Magnetite	Fe_3O_4
Limonite	$Fe_2O_3.3H_2O$
Haemetite	Fe_2O_3

COMMERCIAL FORMS OF IRON

Name	% of carbon
Pig iron or cast iron	2.5 to 4.5%
Wrought iron	0.12 to 0.25%
Steel	0.25 to 2.5%

WROUGHT IRON

Composition

Element	%
S	0.2 to 0.15%
Mn	0.25%
P	0.04 to 0.2%
Fe	Rest

Manufacturing

- Prepared from cast iron in puddling furnace.
- Haemetite ore is used
- Haemetite lining gives oxygen for the oxidation of C, S, Si, Mn and P present in cast iron.
- Oxides of Mn, P, Si and S forms slags($MnSiO_3$),($FePO_4$)
- Hammering is done on balls or blooms to remove slag

STEEL

- Steel is an alloy of Iron containing 0.25 to 2.5% carbon and traces of S,P,Si.

Types of steel

Mild steel	Medium carbon steel	High carbon steel
C=0.1to 0.2%	C=0.2 to 0.7%	C=0.7 to 1.5%
Fairly soft	Harder than mild	More Hard
Malleable and ductile	Malleable and ductile	Forged less than 1% C and cannot forged more than 1% C
Nuts, bolts, bars, boiler, plates are prepared	Making rails, axes, casting are prepared	A hammer, taps, dyes, cutting tools, machine tools, hand steel parts of machine are prepared.

- Steel can be prepared:
  - By removing C, S, P and Si from cast iron
  - Adding Ferromanganese to wrought iron according to the type of steel.

Manufacturing

Two methods are common

1. Open hearth process.
2. Bessemer's process.

Open Hearth Process

- It is a modern method, carried out in open-hearth furnace.
- Open-hearth process is of two types.
  - Furnace with acidic lining e.g .SiO_2, when impurities are Mn, Si
  - Furnace with basic lining e.g. CaO, MgO, when impurities are S and P
- Mixture of cast iron, scrap steel, quick lime heated at 1600°C in furnace

- C is removed in the form of CO
- SiO_2 combines with CaO, MgO and FeO to form slag.
- P and S reacts with Fe_2O_3 and CaO to form slag
- Slag contains $Ca_3(PO_4)_2$ sold as fertilizer.

Bessemer's Process

- Oxides of C, Si and Mn form slag($MnSiO_3$).
- CO burns at mouth of furnace with blue flame.
- Ferromanganese is added to correct the proportion of C when CO flame dies.
- Mn imparts hardness and tensile strength.
- To remove bubbles of O_2, N_2 and CO_2, Al or ferrosilicon is added.

CORROSION

Chemical decay of metal due to action of surrounding medium is called corrosion.

- Water is main source of corrosion.
- Impurities in metal promote corrosion.
- When metal (Al) comes in contact with less active metal (Cu), a galvanic cell is produced.
- Active metals are corroded rapidly due to oxidation than less active metal.

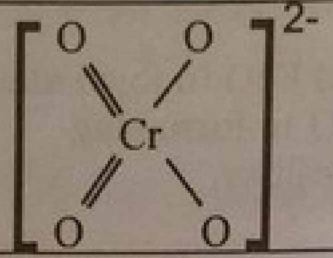
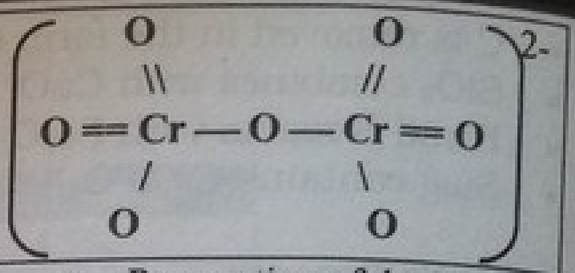
PREVENTION OF CORROSION

- ¼th of iron's total production is damaged due to corrosion.
- We can prevent it by:
  - Coating of oil, paint varnish or enamel
  - Coating of metal with thin layer of another metal (electroplating)
  - Alloy formation.

Tin plating (cathode coating)	Zinc coating (anode coating)
Iron sheet is dipped in molten tin and then passed through hot pairs of roller	Iron sheet is dipped in $ZnCl_2$ and rolled in Zn bath and air-cooled.
Galvanic cell is formed when tin (Sn) layer is damaged	Galvanic cell is formed when Zn is damaged
Tin (Sn) acts as cathode	Fe acts as cathode
Fe acts as anode	Zn acts as anode
Electrons flow from Fe to tin (Sn)	Electron flow from Zn to Fe
Fe decays	Zn decays
	Its corrosion is called sacrificial corrosion as zinc sacrifice.

CHROMATES AND DICHROMATES

Particulars	Chromates	Dichromates
Origin	Salt of chromic acid	Salt of dichromic acid
Preparation	- Oxidation of trivalent Cr with alkalis - By fusing Cr_2O_3 and alkali in presence of $KClO_3$ - By heating natural chromite ($FeO.Cr_2O_3$) with K_2CO_3 in presence of O_2	- From chromates in presence of H_2SO_4 - By converting $Na_2Cr_2O_7$ to $K_2Cr_2O_7$ on reaction with KCl
Colour and state	Yellow solid	Orange red crystalline solid

Structure		
Uses	Yellow crown paint is prepared	▪ Preparation of dyeing ▪ In leather industry for chrome tanning
Oxidizing agent		▪ Changes H_2S in S ▪ $FeSO_4$ to $Fe_2(SO_4)_3$ ▪ KI to I_2

POTASSIUM PERMAGNATE ($KMnO_4$)

Particulars	Description
Preparation	1. by the reaction of H_2SO_4 and K_2MnO_4(Potassium mangnate) 2. from mineral pyrolusite (MnO_2) ▪ finally powdered mineral reacts with KOH in air and oxidizing agent ▪ K_2MnO_4 is formed in fused state ▪ $KMnO_4$ is produced by following methods ❖ **STADELER'S METHOD** ➢ Cl_2 .s passed, which oxidizes K_2MnO_4(green) to $KMnO_4$ (purple) ➢ By the reaction of CO_2 and K_2MnO_4 ❖ **ELECTROLYTIC OXIDATION PROCESS** ➢ During electrolysis, O_2 is produced on anode ➢ This O_2 oxidizes the manganate into permanganate ➢ Purple solution of $KMnO_4$ is filtered through asbestos
Colour	▪ Dark purple lustrous crystal
Solubility	▪ Soluble in water 7% at 20°C, 25% at 63°C
Oxidizing agent	▪ Oxidizes H_2S to S, $FeSO_4$ to $Fe_2(SO_4)_3$ ▪ Oxidizes oxalic acid to CO_2 and H_2O ▪ When reacted with KOH and temperature rises, then O_2 liberates
Usage	▪ As oxidizing agent ▪ Many organic compounds are prepared ▪ As disinfectants and germicides

GARDEN OF EQUATIONS

POTASSIUM PERMANGANATE

Preparation

On small scale

$$3K_2MnO_4 + 2H_2SO_4 \longrightarrow 2K_2SO_4 + 2KMnO_4 + MnO_2 + 2H_2O$$

On large scale

- Stadeler's Process

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$$

- Electrolytic Oxidation Process

$$2K_2MnO_4 + H_2O + [O] \longrightarrow 2KMnO_4 + 2KOH$$

- CO_2 Process

$$3\,K_2MnO_4 + H_2O + CO_2 \longrightarrow 2KMnO_4 + 4KHCO_3 + MnO_2$$

Chemical Reactions Of Potassium Permanganate

$4KMnO_4 + 4KOH \longrightarrow 4K_2MnO_4 + 2H_2O + O_2$

$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$

$2KMnO_4 + 5H_2S + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5S + 8H_2O$

$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$

POTASSIUM DICHROMATE

Preparation

- ☐ $2K_2CrO_4 + H_2SO_4 \longrightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$
- ☐ $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$

Chemical Reactions Of Potassium Dichromate

$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$

$K_2Cr_2O_7 + 4H_2SO + 3H_2S \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3S + 7H_2O$

$K_2Cr_2O_7 + 7H_2SO_4 + 6KI \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O$

$K_2Cr_2O_7 + 6H_2SO_4 + 4NaCl \longrightarrow 2KHSO_4 + 2CrO_2Cl_2 + 4NaHSO_4 + 3H_2O$

POTASSIUM CHROMATE

Preparation

- ☐ $2K_2CrO_4 + 3Br_2 + 8KOH \longrightarrow 2K_2CrO_4 + 6KBr + 4H_2O$
- ☐ $Cr_2O_3 + KClO_3 + 4KOH \longrightarrow 2K_2CrO_4 + KCl + 2H_2O$
- ☐ $4FeCr_2O_3 + 8K_2CO_3 + 9O_2 \longrightarrow 8K_2CrO_4 + 2Fe_2O_3 + 8CO_2$

PRACTICE EXERCISE

20 mins
Time Yourself

1. Co-ordination number of the transition element in $[Pt\ Cl\ NO_2\ (NH_3)_4]^{2-}$ is
   (a) 2
   [✓ (b) 6]
   (c) 4
   (d) 8
2. $K_2(Cu(CN)_4)$ which one is correct
   (a) Potassium tetra cyano cupperate
   (b) Co-ordination number is 2
   (c) Ligand is positively charged
   [✓ (d) Central atom is present in anionic sphere]
3. The oxidation number of central metal atom in $[Ni(CO)_4]$ is
   (a) 0
   (b) 2
   (c) 4
   (d) 6
4. Group VIB of transition elements contains
   (a) Zn, Cd, Hg
   (b) Fe, Ru, Os
   (c) Cr, Mo, W
   (d) Mn, Te, Re
5. The elements in which d or f orbitals are in the process of completion are
   (a) outer transition elements
   (b) inner transition elements
   (c) typical transition elements
   (d) transition elements
6. The location of transition elements is in between
   (a) lanthanides & actinides
   (b) s and p block elements
   (c) chalcogens and halogens
   (d) d and f block elements
7. The melting points and boiling points upto middle of 3d- series
   (a) increases
   (b) decreases
   (c) remain same
   (d) no regular trend
8. Pure metal
   (a) corrode slowly
   (b) corrode rapidly
   (c) does not corrode easily
   (d) none of these
9. Compounds attracted by applied strong magnetic field are called
   (a) diamagnetic
   (b) paramagnetic
   (c) good conductor
   (d) ferromagnetic
10. The correct electronic configuration of 'Cr' is
    (a) $[Ar]4s^2 3d^4$
    (b) $[Ar]\ 4s^2 3d^4$
    (c) $[Ar]4s^0 3d^5$
    (d) $[Ar]\ 4s^1 3d^5$
11. The oxidation state of transition elements is usually
    (a) variable
    (b) constant
    (c) single
    (d) infinite
12. When light is exposed to transition element, then electrons jump from lower orbitals to higher orbitals in
    (a) orbitals of f-subshell
    (b) orbitals of d-subshell
    (c) orbitals of p-subshell
    [✓ (d) both a & b]
13. Non-stoichiometric compounds of transition elements are called
    (a) hydrates
    (b) hydrides
    (c) binary compounds
    (d) interstitial compounds

Na Mg S T V Cr

[Ne] $3s^2, 3d^5$

3s 3p 3d
3s 3p d
4s 4p d

14. When a compound of transition element is dissolved in a solution of salt, then it produces
(a) simple ions
[✓ (b) complex ions]
(c) double salts
(d) strong anions

15. The specie which donates electrons to central metal atom in co-ordination sphere is called
(a) anion
(b) cation
[✓ (c) ligand]
(d) acid

16. The species which donate two electron pairs in a coordination compound is called
(a) ligand
(b) mono-dentate ligand
(c) poly-dentate ligand
[✓ (d) bi-dentate ligand]

17. Which of the following can form a chealate
(a) ammine
[✓ (b) oxalato]
(c) carbonyl
(d) cyano

18. The central atom along with ligands is called
(a) complex ion
[✓ (b) coordination sphere]
(c) ligand
(d) complex compound

19. The compound or complex ion which has a ring in its structure
(a) polydentate ligand
[✓ (b) chelate]
(c) monodentate ligand
(d) hydrate

20. In complex compounds, the oxidation number is written in
(a) English
(b) Greek
[✓ (c) Roman numeral]
(d) Hebrew

21. Geometry of the complex compounds usually depends upon
(a) type of ligands
[✓ (b) types of hybridization in the elements of ligands]
(c) hybridization of central metal
(d) All of above

22. When the central atom of coordination compound is sp^3d^2 hybridization, the expected geometry will be
(a) tetrahedral
(b) square planar
(c) trigonal bipyramidal
[✓ (d) octahedral]

23. In pig iron, the concentration of C-atom is
(a) 0.12 --- 0.25%
[✓ (b) 2.5 --- 4.5%]
(c) 2.0 --- 4.0%
(d) 0.25 ---- 2.5%

24. In the production of wrought iron,Mg,Si and P are removed in the form of
(a) oxides
(b) silicates
[✓ (c) slag]
(d) carbonates

Non metal

25. With impurities like P and S, the open hearth furnace is lined with.
~~(a) SiO_2~~ acidic
(b) Fe_2O_3
(c) FeO
[✓ (d) CaO, MgO]

26. The oxidation number in $[\overset{+6\;-8}{Mn}O_4]^{-2}$
(a) +7
(b) -7
[✓ (c) +6]
(d) -6

27. Which is sold as fertilizer
(a) $CaSiO_3$
(b) Na_2SiO_3
[✓ (c) $Ca_3(PO_4)_2$]
(d) $MnSiO_3$

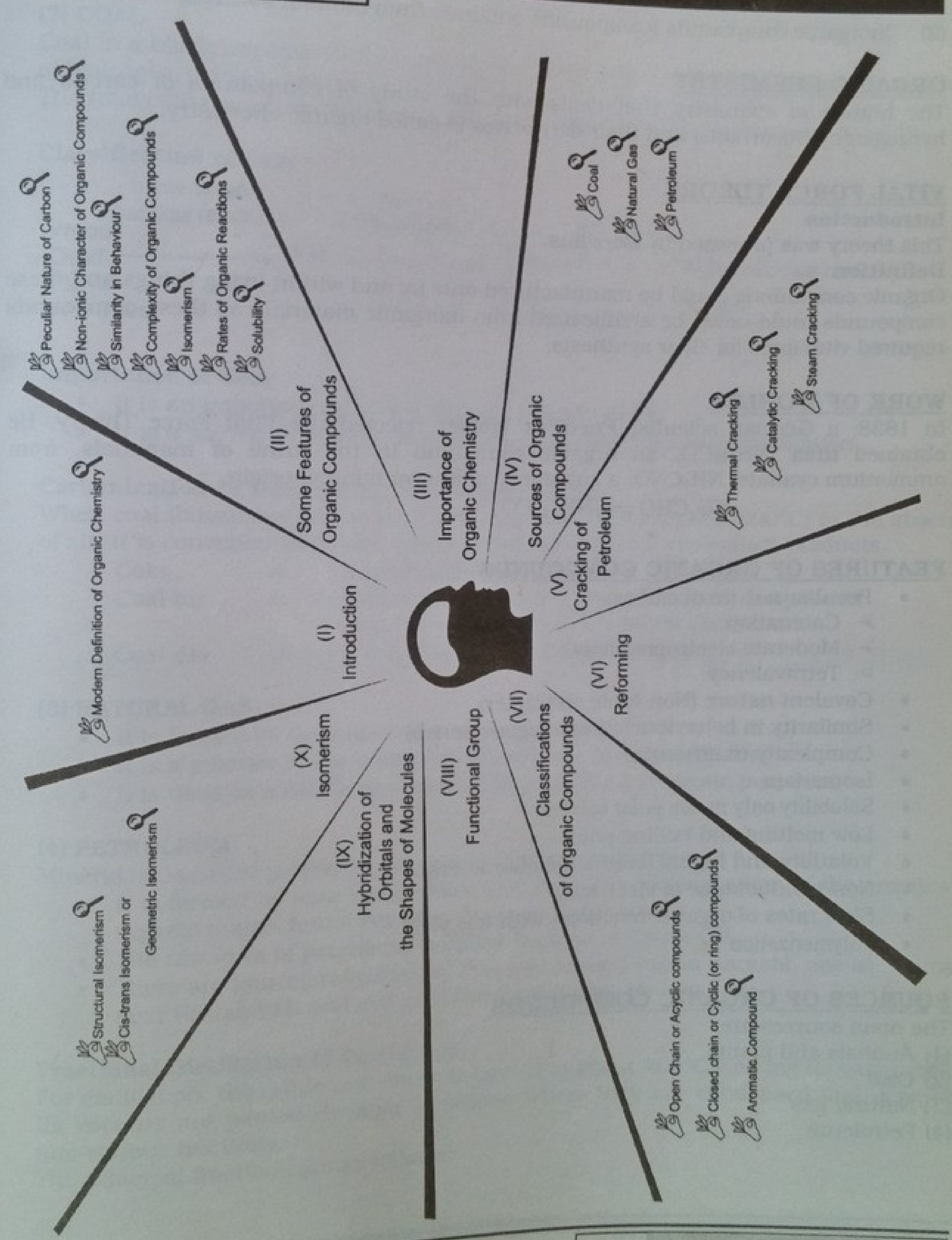
28. Any process of chemical decay of metals due to the action of surroundin
medium is called
(a) activation (b) enameling
[✓ (c) corrosion] (d) coating

29. When an active metal like Al comes in contact with less active element like Cu
then it produces
(a) dry cell [✓ (b) galvanic cell]
(c) electrolytic cell (d) a and b

30. Which of the following is a typical transition metal?
(a) Sc (b) Y
(c) Cd [✓ (d) Co]

Chapter 7

FUNDAMENTAL PRINCIPLES OF ORGANIC CHEMISTRY


(I) Introduction
Modern Definition of Organic Chemistry
(II) Some Features of Organic Compounds
Peculiar Nature of Carbon
Non-ionic Character of Organic Compounds
Similarity in Behaviour
Complexity of Organic Compounds
Isomerism
Rates of Organic Reactions
Solubility
(III) Importance of Organic Chemistry
(IV) Sources of Organic Compounds
Coal
Natural Gas
Petroleum
(V) Cracking of Petroleum
Thermal Cracking
Catalytic Cracking
Steam Cracking
(VI) Reforming
(VII) Classifications of Organic Compounds
Open Chain or Acyclic compounds
Closed chain or Cyclic (or ring) compounds
Aromatic Compound
(VIII) Functional Group
(IX) Hybridization of Orbitals and the Shapes of Molecules
(X) Isomerism
Structural Isomerism
Cis-trans Isomerism or Geometric Isomerism

INTRODUCTION

On the basis of origin, chemical compounds were classified as
(1) Organic compounds (compounds obtained from living things)
(2) Inorganic compounds (compounds obtained from mineral sources)

ORGANIC CHEMISTRY

The branch of chemistry that deals with the study of compounds of carbon and hydrogen(hydrocarbons) and their derivatives is called organic chemistry.

VITAL FORCE THEORY

Introduction

This theory was proposed by Berzilius.

Definition

Organic compounds could be manufactured only by and within living things and these compounds could never be synthesized from inorganic materials as these compounds required vital force for their synthesis.

WORK OF WOHLER

In 1828, a German scientist Friedrick Wohler rejected the Vital Force Theory. He obtained urea $(NH_2)_2CO$, an organic compound in the urine of mammals, from ammonium cyanate, NH_4CNO, a substance of known mineral origin.

$$NH_4CHO \rightleftharpoons (NH_2)_2CO$$

FEATURES OF ORGANIC COMPOUNDS

- Peculiar nature of carbon
  - Catenation
  - Moderate electropositivity
  - Tetravalency
- Covalent nature (Non-ionic character)
- Similarity in behaviour (homologous series)
- Complexity in structure
- Isomerism
- Solubility only in non polar solvents
- Low melting and boiling points
- Volatility and highly flammable characters
- Non-conductance of electricity
- Slow rates of organic reactions with low yield
- Polymerization

SOURCES OF ORGANIC COMPOUNDS

The main sources are
(1) Animals and plants
(2) Coal
(3) Natural gas
(4) Petroleum

Chapter 7 Fundamental Principles of Organic Chemistry

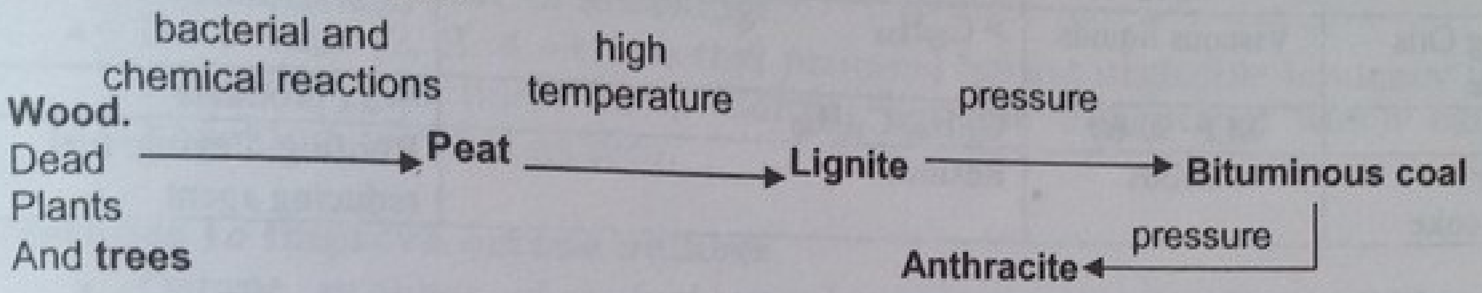
(1) Animals and plants

Proteins, carbohydrates, fats, oils, enzymes etc are organic compounds obtained from animals and plants.

(2) COAL

Coal is a black mineral of vegetable origin consisting of carbon with minute amounts of hydrogen, oxygen, nitrogen and sulphur.
The total coal resources of Pakistan are estimated about 184 billion tonnes.

Classification of Coal



Importance of Coal

- It is an important solid fuel (80% in baking bricks)
- It is a source of organic compounds when subjected to carbonization.

Carbonization or Destructive Distillation of Coal

When coal (bituminous) is heated to a high temperature (500-1000°C) in the absence of air, it is converted into coke, coal gas and coal tar and many such products.

Coke ⇒ a good reducing agent
Coal tar ⇒ contains about 215 types of aromatic compounds that we can extract by fractional distillation.
Coal gas ⇒ it contains CH_4, CO and H_2 gases.

(3) NATURAL GAS

- It is formed by decomposition of organic matter.
- It is a mixture of low boiling hydrocarbons, mainly methane.
- It is used as a fuel in general industries and for domestic purposes.

(4) PETROLEUM

Mineral oil is called petroleum when it is in the refined form

- It is formed by slow biochemical and chemical decomposition of the remains of organic matter found between the sedimentary rocks.
- The raw form of petroleum is called Rock oil or Crude Oil.
- There are four oil refineries in Pakistan located two in Karachi, one at Morgah near Rawalpindi and one at Mahmud Kot near Multan.

Fractional Distillation of Petroleum

For distillation, the crude petroleum is heated to about 400°C causing its vaporization. Its vapours are passed through a column where they are condensed and separated into various fractions.
The principal fractions are as follows: -

Fraction	Boiling Point Range (°C)	Composition	Uses
Natural gas	< 20	CH_4-C_4C_{10}	Fuel, petrochemicals
Petroleum ether	20-60	C_5H_{12},C_6H_{14}	Solvent
Ligroin, or naphtha	60-100	C_6H_{14},C_7H_{16}	Solvent, raw material
Gasoline	40-220	C_4H_{10}-$C1_3H_{28}$ mostly C_6H_{14}-C_8H_{18}	Motor fuel
Kerosene	175-325	C_8H_{18}-$C1_4H_{30}$	Heating fuel
Gas Oil	>275	$C_{12}H_{26}$-$C_{18}H_{38}$	Diesel and heating fuel
Lubricating Oils and greases	Viscous liquids	> $C_{18}H_{38}$	Lubrication
Paraffin	M.P. 50-60	$C_{23}H_{48}$-$C_{29}H_{60}$	Wax products
Asphalt, or petroleum coke	Solids	Residue	Roofing. Paving, fuel reducing agent

CRACKING OF PETROLEUM

- The break down of larger hydrocarbons into smaller and more volatile hydrocarbons having low boiling points is called cracking.
- Oil fractions are purposely cracked to yield gasoline because of its high demand (petroleum yields only about 20%).
- Cracking breaks C-C or C-H bond at any point e.g.

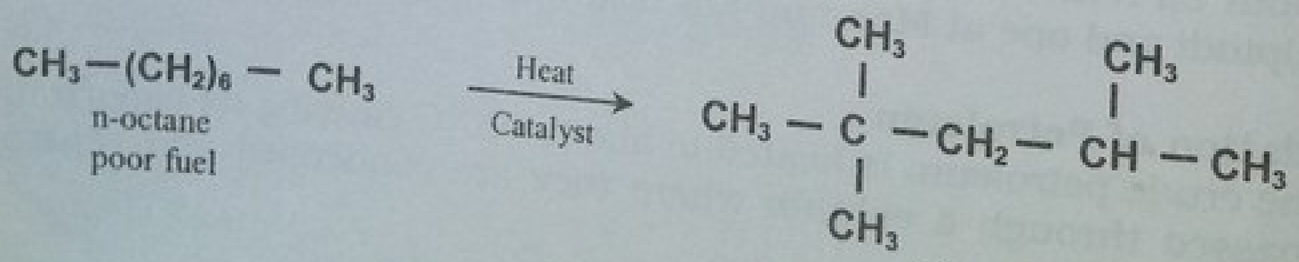
$$\underset{\text{Hexadecane}}{C_{16}H_{34}} \xrightarrow[700^\circ C]{\text{Heat}} C_7H_{16} + C_2H_4 + CH_3-CH=CH_2$$

- There are three ways to carry out cracking:

	Thermal	Catalytic	Steam
Additive	-	Aluminosilicates	Steam
Temperature	High	Lower (500°C)	First 900°C, then cool rapidly
Pressure	High	Lower (2atm)	-
Uses	Production of higher unsaturated hydrocarbons	Production of better quality gasoline i.e. of high octane number	Production of lower unsaturated hydrocarbons

REFORMING

It is the conversion of straight chain hydrocarbons into branched chain hydrocarbons in order to increase octane number of a fuel.



$$\underset{\substack{\text{n-octane}\\\text{poor fuel}}}{CH_3-(CH_2)_6-CH_3} \xrightarrow[\text{Catalyst}]{\text{Heat}} CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-CH_2-\overset{\overset{\large CH_3}{|}}{CH}-CH_3$$

iso-octane (good fuel)
2,2,4-trimethyl pentane

Knocking:

It is a sharp metallic sound produced in internal combustion engine because of premature ignition of petrol – air mixture before the spark plug fires.

Octane Number:

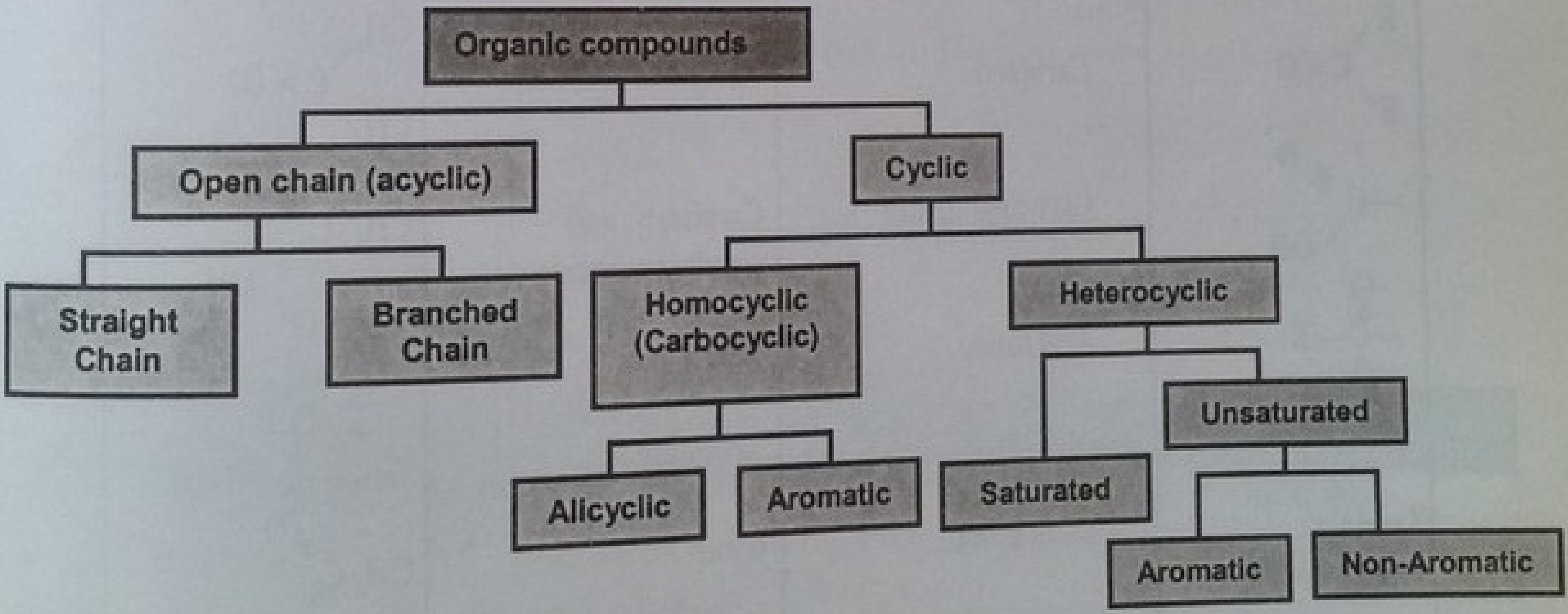
Octane Number of a particular motor fuel is defined as the percentage of iso-octane in a mixture of iso-octane and n-heptane which gives equivalent knock performance.

- It gives a measure of knocking.
- Iso-octane (2, 2, 4 – tri methyl pentane) having negligible tendency to knock is rated as 100 (ideal fuel]. Normal heptane (n-heptane) which causes great knocking, is rated as zero.

Methods to improve octane number

- Octane number of a fuel can be increased by adding small amounts of antiknock compounds e.g. Tetra ethyl lead (TEL). Such compounds acts as knock inhibitors and moderate the explosions in the cylinders of engine.TEL creates air pollution as its compound are toxic. e.g.PbO, $PbCO_3$.
- Cracking
- Isomerization
- Addition of cyclic compounds

CLASSIFICATION OF ORGANIC COMPOUNDS



FUNCTIONAL GROUP

An atom or a group of atoms or a double bond or a triple bond whose presence imparts specific properties to organic compounds is called a functional group.

Characteristics

- Each functional group defines an organic family.
- They are the chemically functional parts of molecules.
- Although over six million organic compounds are known, there are only a handful of functional groups.

Functional group		Class of compounds	Example
Formula	Name		
$-\overset{\mid}{\underset{\mid}{C}}-\overset{\mid}{\underset{\mid}{C}}-$	None	Alkane	CH_3-CH_3
$>C=C<$	Double bond	Alkene	$H_2C=CH_2$
$-C\equiv C-$	Triple bond	Alkyne	$HC\equiv CH$
-X(X=F,Cl,Br,I)	Halo (fluoro, chloro, bromo, iodo)	Alkyl halide	CH_3-CH_2-Cl
$-OH$	Hydroxyl group	Alcohol or alkanol	CH_3-CH_2-OH
$-NH_2$	Amino group	Amine	$CH_3-CH_2-NH_2$
$>C=NH$	Imino group	Imine	$CH_2=NH$
$-\overset{\mid}{\underset{\mid}{C}}-O-\overset{\mid}{\underset{\mid}{C}}-$	Ether linkage	Ether	$CH_3-CH_2-O-CH_2-CH_3$
$-C\overset{\nearrow O}{\underset{\searrow H}{}}$	Formyl group	Aldehyde or alkanal	$CH_3-C\overset{\nearrow O}{\underset{\searrow H}{}}$
$\overset{R\searrow}{\underset{R\nearrow}{}}C=O$	Carbonyl	Ketone or alkanone	$\overset{CH_3\searrow}{\underset{CH_3\nearrow}{}}C=O$
$-C\overset{\nearrow O}{\underset{\searrow OH}{}}$	Carboxyl group	Carboxylic acid (or alkanoic acid)	$CH_3-C\overset{\nearrow O}{\underset{\searrow OH}{}}$
$-\overset{O}{\overset{\parallel}{C}}-X$	Acid halide	Acid halide	$CH_3-\overset{O}{\overset{\parallel}{C}}-Cl$
$-\overset{O}{\overset{\parallel}{C}}-NH_2$	Acid amide	Acid amide	$CH_3-\overset{O}{\overset{\parallel}{C}}-NH_2$
$R-C\overset{\nearrow O}{\underset{\searrow OR}{}}$	Ester group	Ester	$CH_3-C\overset{\nearrow O}{\underset{\searrow OCH_3}{}}$
$-SH$	Mercapto	Thioalcohol or Thiol	CH_3-CH_2-SH
$-C\equiv N$	Cyano	Alkyl cyanide or alkane nitrile	$CH_3-C\equiv N$
$-N\overset{\nearrow O}{\underset{\searrow O}{}}$	Nitro	Nitro compounds	$C_6H_5NO_2$

Chapter 7

Fundamental Principles of Organic Chemistry

HYBRIDIZATION OF ORBITALS AND THE SHAPES OF MOLECULES

Property	Methane	Ethane	Ethene	Ethyne
Hybridization	sp^3	sp^3	sp^2	sp
Shape	Tetrahedron	Double tetrahedron	Planar trigonal	Linear
Angle	109.5°	109.5°	120°	180°
σ-bonds	4	7	5	3
π-bonds	0	0	1	2

ISOMERISM (Iso = same ; Merose = units)

Two or more compounds having same molecular formula but different structures are called isomers and the phenomenon is known as isomerism.

- In saturated hydrocarbons methane, ethane & propane (amongst alkanes) have one structural form only i.e. no isomerism
- Isomerism is possible for compounds having at least *three carbon atoms.*
- Number of isomers increases with increase in number of carbon atoms in saturated hydrocarbon.

No. of carbons	No. of Isomers
4	2
5	3
6	5
7	9
8	18
9	35
10	75

TYPES OF ISOMERISM

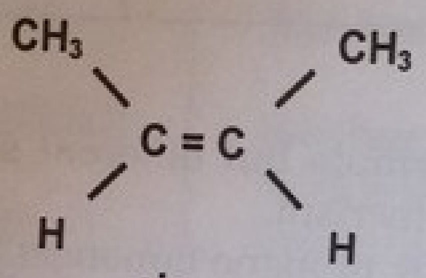
A. Structural Isomerism

Type	Reason of isomerism	Functional groups	Example
Chain or skeletal isomerism	Difference in nature of carbon chains	Same	n-pentane, iso-pentane & neo-pentane
Position isomerism	Difference in position of same functional group on the carbon chain	Same	1-butene & 2- butene
Functional group isomerism	Same molecular formula, but different functional groups	Different	propanal & propanone
Metamerism	Unequal distribution of carbon atoms (R) on either side of functional group	Same	diethyl ether & methyl n-propyl ether

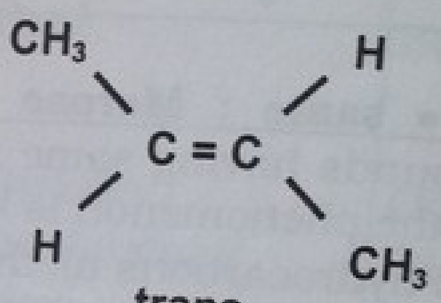
B. Cis-Trans Isomerism or Geometric Isomerism

Two compounds that possess the same structural formula but differ with resp the positions of the identical groups in space are cis-trans isomers.

- **Reason:** Two carbon atoms with double bond cannot rotate freely, ho relative position of the attachments get fixed.
- **Condition:** Two groups attached to same carbon atom must be different. In cis form, similar groups lie on same side of double bond while in trans f similar groups lie on opposite sides of double bond.
- **Example:** 2-butene



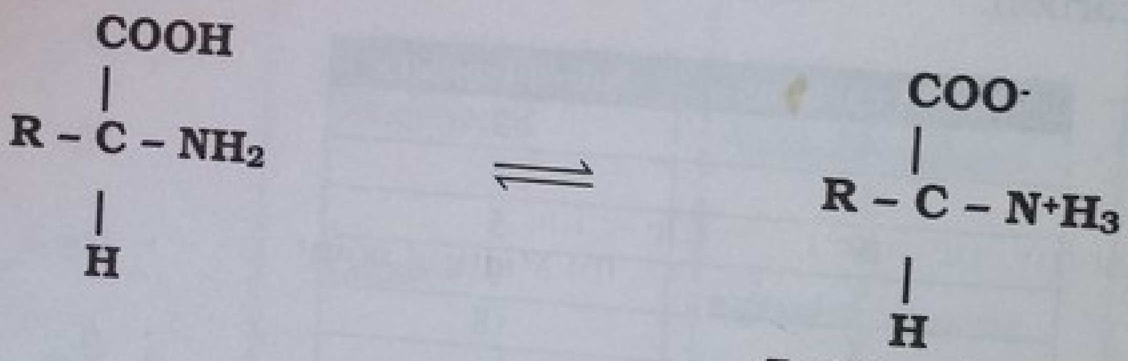
cis



trans

C. Tautomerism

This type of isomerism arises due to shifting of proton from one atom to other in th same molecule.



Zwitter ion

DIFFERENCE BETWEEN HOMOLOGUES AND ISOMERS

	Homologues	Isomers
General formula	Applicable	No
Functional group	Same	May or may not be same
Periodic difference of CH_2	Present	Absent
Structural formula	Similar	Different
Molecular formula	Different	Same
Molecular weight	Different	Same

Chapter 7

Fundamental Principles of Organic Chemistry

PRACTICE EXERCISE

30 mins
Time Yourself

1. Main source of organic compounds is
(a) Animal
(b) Fossil
(c) Coal
(d) Plants
2. Octane number can be improved by
(a) Isomerization
(b) Adding $(C_2H_5)_4Pb$
(c) Adding $(CH_3)_4Pb$
(d) All
3. Hydro carbons which burn with smoky flame are called
(a) Aliphatic
(b) Alicyclic
(c) Aromatic
(d) Aldehyde
4. Octane number 2,2,4-trimethyl pentane is
(a) 100
(b) 90
(c) 80
(d) 70
5. Propene can exhibit
(a) cis-trans isomerism
(b) geometric isomerism
(c) both a & b
(d) none of the above
6. Geometric isomerism is usually found in
(a) Alkanes
(b) Alkenes
(c) Alkynes
(d) Esters
7. Pentane and 2-methyl butane have the same
(a) Boiling point
(b) Melting point
(c) Percentage composition
(d) Structural formula
8. Organic compounds that are essentially nonpolar and exhibit weak intermolecular forces have
(a) Low melting points
(b) Low vapour pressure
(c) High boiling points
(d) High electrical conductivity
9. The first organic compound was synthesized in laboratory by
(a) Wohler
(b) Kolbe
(c) Berzilius
(d) Berthelot
10. According to vital force theory
(a) organic compounds can be synthesized from inorganic compounds
(b) organic compounds cannot be synthesized from inorganic compounds
(c) organic compounds can be synthesized by animals
(d) organic compounds can be synthesized by plants
11. First organic compound synthesized in laboratory was
(a) tartaric acid
(b) ethyl alcohol
(c) methanol
(d) urea
12. A double bond consists of
(a) Two sigma bonds
(b) Two Pi bonds
(c) One sigma and one Pi bond
(d) One sigma and two Pi bonds
13. The property of carbon chain formation is called
(a) catenation
(b) hybridization
(c) polymerization
(d) solvation

14. Chemical properties of first member of homologous series with respect to other members are
(a) same (b) different
(c) depends upon number of C atoms (d) depends upon number of H atoms

15. The organic compounds having very high molecular weight are called
(a) carboxylic acids (b) ketones
(c) aldehydes (d) polymers

16. Compounds having same molecular formula but differ in structural formula are called
(a) polymer (b) monomer
(c) isomer (d) allotropes

17. Rate of reactions of most organic compounds are
(a) very slow (b) very fast
(c) slow (d) no regular character present

18. Organic compounds are soluble in
(a) polar solvent (b) non-polar solvent
(c) alkalies (d) water

19. Coal is produced after a long time decay of
(a) animals (b) fossils
(c) wood (d) all of the above

20. Methane is used in power generation in chemical industries being a
(a) natural gas (b) good caloric value
(c) cheaper (d) All

21. Crude oil is blackish coloured liquid produced after the decay of organic matter present between
(a) earth layer (b) mountains
(c) sedimentary rocks (d) rocks

22. The process in which larger molecule with higher molecular weight breaks down into smaller molecules with lower molecular weight
(a) polymerization (b) pyrolysis
(c) isomerism (d) no such process occurs

23. At low temperature and pressure, cracking can be done in presence of catalyst
(a) Al_2O_3 (b) Fe_2O_3
(c) Al_2O_3 and SiO_2 (d) Fe_2O_3 and SiO_2

24. The metallic sound produced by engine due to the pre-ignition of fuel is called
(a) knocking (b) reforming
(c) cracking (d) a and c

25. Which one of the following compounds shows intense knocking?
(a) n-pentane (b) iso-heptane
(c) iso-octane (d) n-heptane

26. Which of the following can be used as anti-knocking agent.
(a) $PbCl_2$ (b) $(C_2H_5)_4Pb$
(c) $(C_2H_5)_2Pb$ (d) All of the above

27. Ether functional group can be represented as
(a) –OH (b) R-CO-R
(c) R-O-R (d) R-COOH

28. Isomerism which is present only in alkene is
(a) structural isomerism
(b) metamerism
(c) cis-trans isomerism
(d) both b and c

29. A single atom or group of atoms which gives, characteristic properties to a compound is called
(a) radical
(b) hydrocarbon
(c) functional group
(d) ion

30. Compound containing benzene ring in their structure are
(a) aliphatic
(b) aromatic
(c) carboxylic acid
(d) carbohydrates

31. 2-propanol and 1-propanol show the isomerism
(a) metamerism
(b) functional group isomerism
(c) geometric isomerism
(d) position isomerism

32. Which of the following is an amide
(a) $R\text{-}NH_2$
(b) $RCONH_2$
(c) $R-NH-R$
(d) $C_6H_5NH_2$

33. In sp^3 hybridization, the expected geometry of molecules will be
(a) square planar
(b) trigonal pyramidal
(c) tetrahedral
(d) linear

34. Only sigma bonds are present in
(a) propene
(b) butanoic acid
(c) butanal
(d) ethoxy ethane

35. In cyano group the carbon atom shows which kind of hybridization.
(a) sp^2
(b) sp
(c) sp^3
(d) none of the above

36. The structure of ethyne is
(a) angular
(b) trigonal
(c) linear
(d) trigonal planar

37. the fractional distillation of petroleum produces gasoline up to
(a) 10%
(b) 15%
(c) 20%
(d) 30%

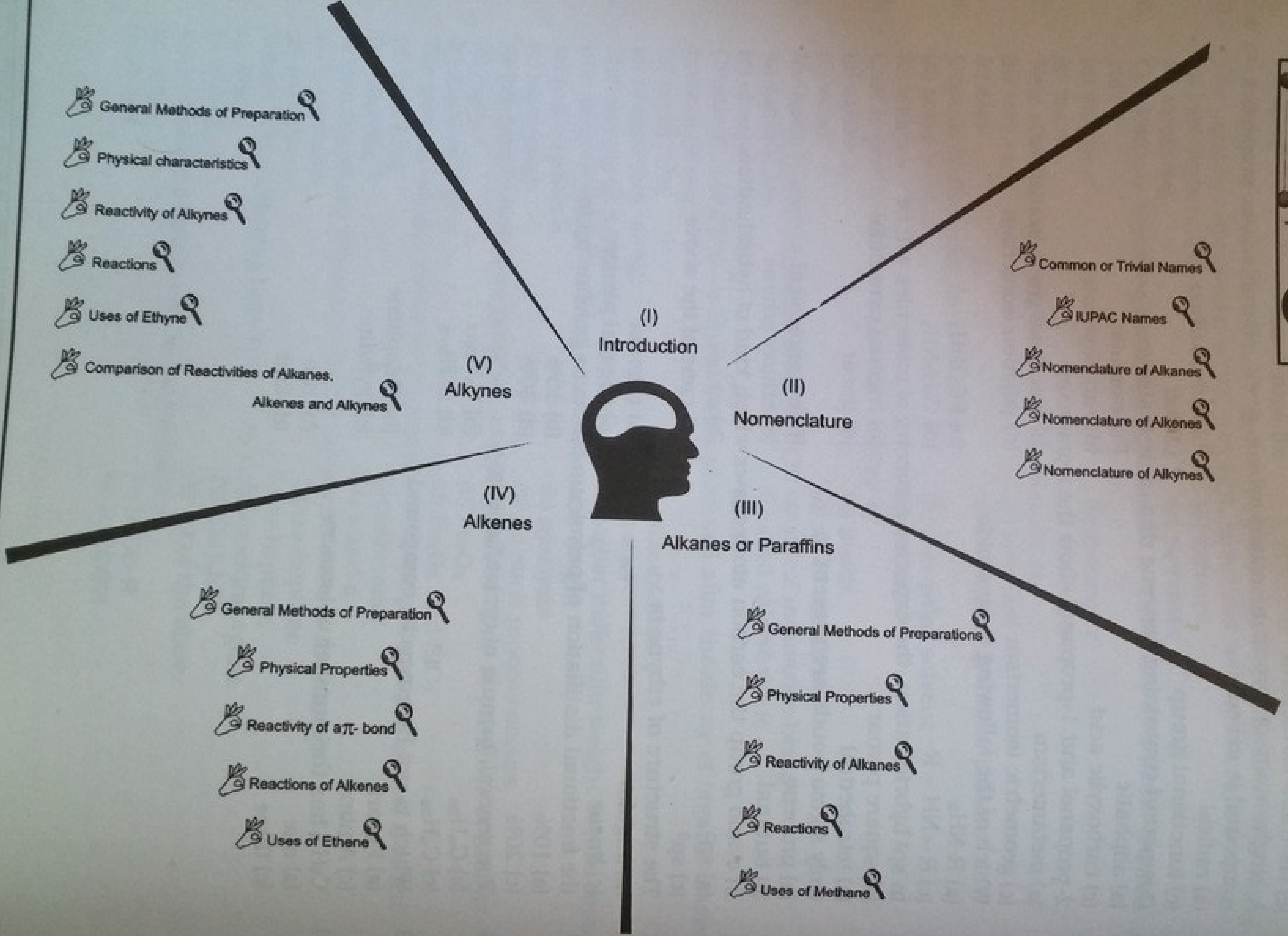
38. The general formula of cycloalkene is
(a) C_nH_{2n}
(b) C_nH_{2n+2}
(c) C_nH_{2n-1}
(d) C_nH_{2n-2}

39. Which is not heterocyclic compound
(a) Furan
(b) Thiophene
(c) Aniline
(d) Pyridine

40. C_5H_{12} has the number of isomers
(a) one
(b) two
(c) three
(d) four

Chapter 8

ALIPHATIC HYDROCARBONS



(I) Introduction

(II) Nomenclature

- Common or Trivial Names
- IUPAC Names
- Nomenclature of Alkanes
- Nomenclature of Alkenes
- Nomenclature of Alkynes

(III) Alkanes or Paraffins

- General Methods of Preparations
- Physical Properties
- Reactivity of Alkanes
- Reactions
- Uses of Methane

(IV) Alkenes

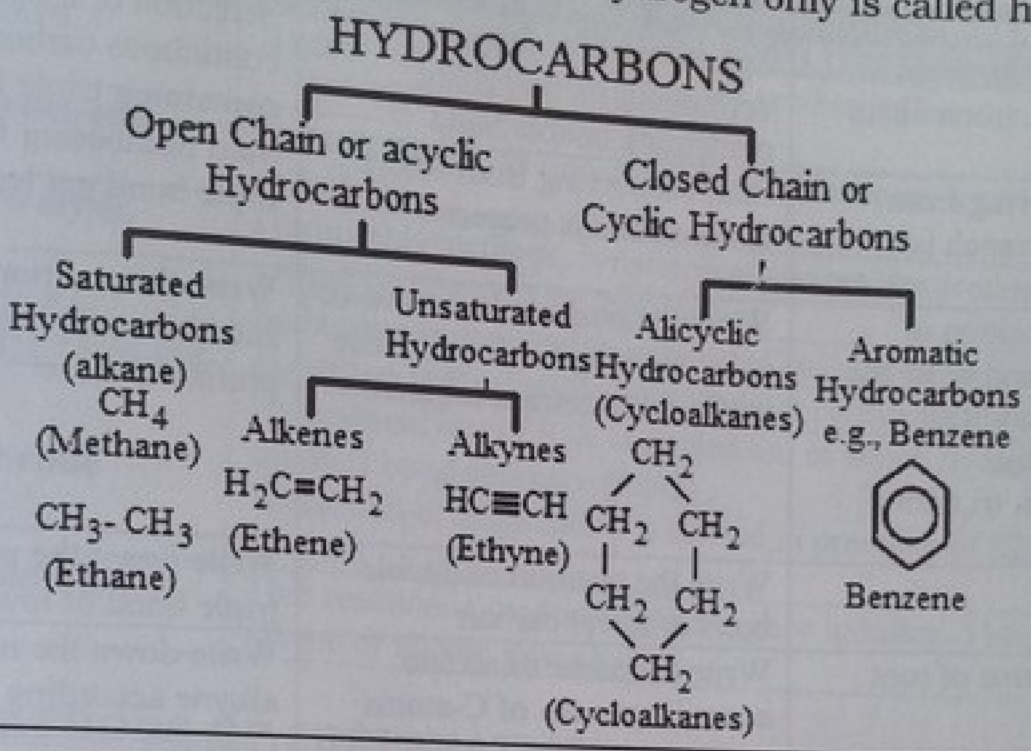
- General Methods of Preparation
- Physical Properties
- Reactivity of a π- bond
- Reactions of Alkenes
- Uses of Ethene

(V) Alkynes

- General Methods of Preparation
- Physical characteristics
- Reactivity of Alkynes
- Reactions
- Uses of Ethyne
- Comparison of Reactivities of Alkanes, Alkenes and Alkynes

HYDROCARBONS

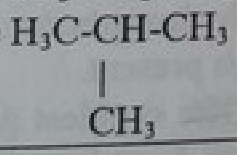
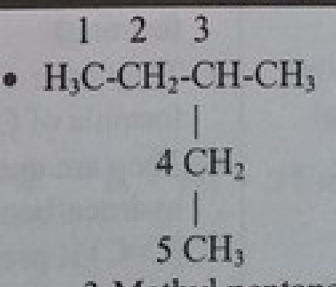
The organic compounds consist of carbon and hydrogen only is called hydrocarbons.



Working for Nomenclature

Year	Progress
1889	Solution was sought for naming organic compounds by IUC
1892	An incomplete report was accepted in Geneva
1930	Modified report was referred as Liege Rules by IUC
1947	IUPAC further modified the report
1979	The report was published

NOMENCLATURE

Common or Trivial Names	IUPAC Names
• Methane (marsh gas) CH_4 • Ethane C_2H_6 • Propane C_3H_8 • Butane C_4H_{10} • n-Pentane $CH_3-CH_2-CH_2-CH_2-CH_3$ • Iso-butane  $H_3C-\underset{\displaystyle CH_3}{\underset{\mid}{CH}}-CH_3$	•  $\overset{1}{H_3C}-\overset{2}{CH_2}-\overset{3}{\underset{\underset{\displaystyle 5\,CH_3}{\underset{\mid}{\underset{\displaystyle 4\,CH_2}{\mid}}}}{CH}}-CH_3$ 3-Methyl pentane

IUPAC Principle For Nomenclature
"Each different compound should have a different name"

Chapter 8 Aliphatic Hydrocarbons

NOMENCLATURE OF ALKANES, ALKANES & ALKYNES

Alkanes	Alkenes	Alkynes
Selection of longest continuous carbon chain	Selection of longest continuous carbon chain containing double bond	Selection of longest continuous carbon chain containing triple bond
Start numbering from where any branch is nearest	Start numbering from where double bond is nearest	Start numbering from where triple bond get least no.
Write the position of substituent and write the name of substituent alphabetically. use prefix di, tri,tetra if required	Write the position and name of substituent alphabetically, use prefix di, tri,tetra if required	Write the position and name of substituent alphabetically, use prefix di, tri, tetra if required
-	Write the position of double bond of lower carbon	Write down the position of triple bond of lower carbon
Write the name of root chain	Write the name of alkene according to no. of C-atoms	Write down the name of alkyne according to the no. of C-atoms
	If there are more than one double bond present then write position of each double bond and ene is replaced with suffix diene, triene and tetraene etc	If there are more than one triple bond, then write down the position of each triple bond and yne is replaced with suffix diyne, triyne, tetrayne etc

GENERAL POINTS FOR ALKANES, ALKENES & ALKYNES

Alkanes	Alkenes	Alkynes
• They are also called paraffins(Latin: Parum = little,Affins=Affinity) • They have a general formula of C_nH_{2n+2} • They are saturated hydrocarbons • Methane (CH_4) is the simplest member of alkane family	• They are also called Olefins (Latin: Olefiant = Oil forming) • They have a general formula of C_nH_{2n} • They are unsaturated hydrocarbons in which (C=C) is present • The simplest olefin is ethene (C_2H_4) • Alkenes having one double bond are called mono-enes while having two double bonds are called dienes.....and so on	• Unsaturated hydrocarbons which contain a triple bond between two carbon atoms are called Alkynes. • They have a general formula of C_nH_{2n-2} • They are unsaturated hydrocarbons in which $C \equiv C$ is present. • The simplest Alkyne is ethyne or Acetylene (C_2H_2)

PREPARATION OF ALKANES

Reaction	Remarks
From Grignard's reagent	Hydrolysis of Grignard's reagent produces alkane.
From aldehydes and ketones	Both reactions are also known as Clemmensen's or Wolf Kishner reduction
Kolbe's electrolysis method	During this methods, symmetrical alkanes are produced and methane cannot be prepared by this method
Decarboxylation of mono-carboxylic acid salt	Soda-lime is prepared by mixing of soaking quick lime (CaO) and caustic soda By distillation of sodium carboxylate with soda lime.
From alkyl halide	Hydrogenolysis of R-X is carried out in which hydrogen is added by the H-H bond cleavage.(Pd/C) Reduction of alkyl halide is carried in presence of (Zn + HCl) reagent.
Sabatier- Sendern's reaction	This reaction is used in vegetable ghee industry. The reduction of alkene or alkyne give alkane

GENERAL METHODS OF PREPARATION

- Decarboxylation of Mono-carboxylic Acid Salts.

$$RCOONa + NaOH \xrightarrow[CaO]{\Delta} R-H + Na_2CO_3$$

- Sabatier – Sendern's Reaction

$$R-CH=CH_2 + H_2 \xrightarrow[200\text{-}300^{\circ}C]{Ni} R-CH_2-CH_3$$

- From alkyl halide

$$R-X + Zn + HX \xrightarrow{HCl} R-H + ZnX_2$$

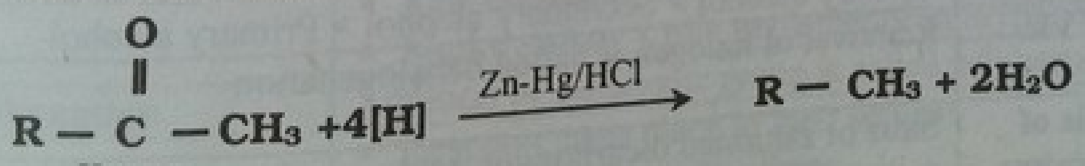
- Kolbe's Electrolytic Method

$$2RCOONa + 2H_2O \xrightarrow{electrolysis} R-R + H_2 + 2NaOH + 2CO_2$$

- From Grignard Reagent

$$R-Mg-X + HOH \xrightarrow[Acid]{H+} R-H + OH-Mg-X$$

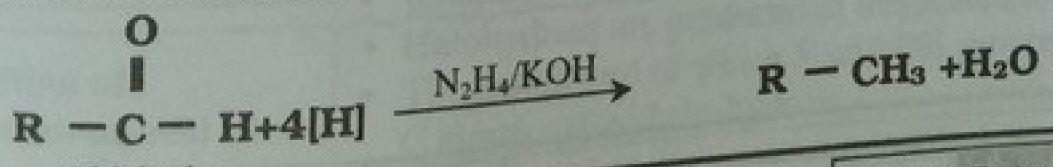
- Clemmensen Reduction



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + 4[H] \xrightarrow{Zn\text{-}Hg/HCl} R-CH_3 + 2H_2O$$

Ketone

- Wolf Kishner Reduction



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H + 4[H] \xrightarrow{N_2H_4/KOH} R-CH_3 + H_2O$$

Aldehyde

REACTIVITY OF ALKANES

They are chemically less reactive and thus also called paraffins.

Reasons for less reactivity

- Electro negativity difference of carbon and hydrogen is only 0.4 non polar
- Inertness of σ–bond neither attack an electrophile nor a nucleophile can attack on them

CHEMICAL OF METHANE

$$\underset{\text{(limited)}}{3CH_4 + 4O_2} \xrightarrow{\text{Flame}} 2CO + 6H_2O + C$$

$$CH_4 + 2O_2 \xrightarrow{\text{Flame}} CO_2 + 2H_2O + 891KJmol^{-1}$$

$$CH_4 + [O] \xrightarrow[\text{400°C, Cu}]{\text{200 atm}} \underset{\text{Methyl alcohol}}{CH_3OH}$$

$$CH_3OH + [O] \xrightarrow[\text{400°C, Cu}]{\text{200 atm}} \underset{\text{Formaldehyde}}{H-CHO} + H_2O$$

$$H-CHO + [O] \xrightarrow[\text{400°C, Cu}]{\text{200 atm}} \underset{\text{Formic acid}}{H-COOH}$$

$$CH_4 + HNO_3 \xrightarrow{\text{400-500°C}} \underset{\text{Nitromethane}}{CH_3-NO_2} + H_2O$$

$$CH_4 + Cl_2 \xrightarrow{h\nu} \underset{\text{Methyl chloride}}{CH_3Cl} + HCl$$

$$CH_3Cl + Cl_2 \xrightarrow{h\nu} \underset{\text{Methylene chloride}}{CH_2Cl_2} + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{h\nu} \underset{\text{Chloroform}}{CHCl_3} + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} \underset{\text{Carbon tetrachloride}}{CCl_4} + HCl$$

PREPARATION OF ALKENES

Reaction	Remarks
Dehydrohalogenation	Removal of hydrogen and halogen from two adjacent carbon atoms is called dehydrohalogenation.
Dehydration of alcohol	▪ Removal of water molecule is called dehydration ▪ Tendency of dehydration is as given below. Tertiary alcohol > Secondary alcohol > Primary alcohol
Dehalogenation of Vic-dihalide	Removal of halogen is called dehalogenation
Kolbe's electrolysis of dicarboxylic acid salts	Salts of saturated dicarboxylic acid are subjected to electrolysis in an aqueous solution and alkenes are formed

Chapter 8

Aliphatic Hydrocarbons

GENERAL METHODS OF PREPARATION

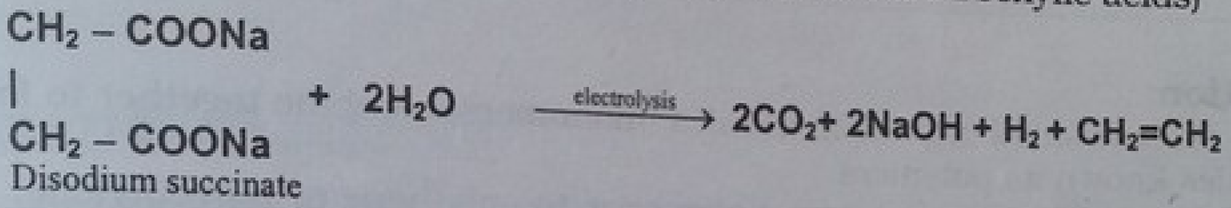
- Dehydration of Alcohols

$$\underset{\text{Alcohol}}{R-CH_2-CH_2-OH} \xrightarrow[340\text{-}450^\circ C]{Al_2O_3} \underset{\text{Alkene}}{R-CH=CH_2} + H_2O$$

- Dehydrohalogenation of Alkyl Halide

$$\underset{\text{Alkyl halide}}{R-CH_2-CH_2-X} \xrightarrow[100^\circ C]{\text{alc.KOH}} \underset{\text{Alkene}}{R-CH=CH_2} + HX$$

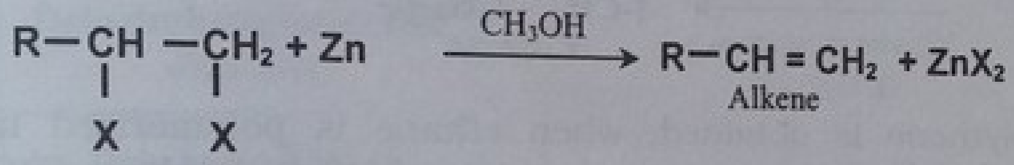
- Kolbe's Electrolytic Method (Electrolysis of salts of dicarboxylic acids)



$$\begin{array}{l} CH_2-COONa \\ | \\ CH_2-COONa \end{array} + 2H_2O \xrightarrow{\text{electrolysis}} 2CO_2 + 2NaOH + H_2 + CH_2=CH_2$$

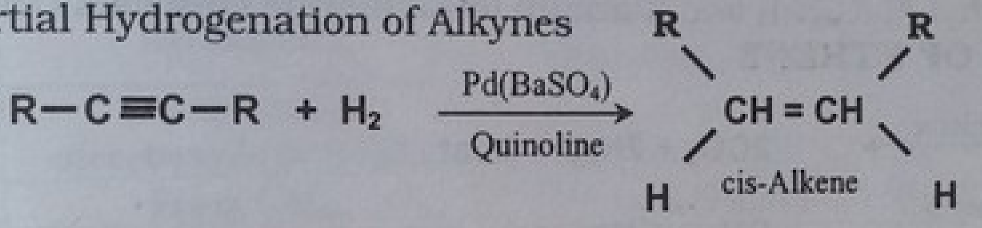
Disodium succinate

- Dehalogenation of Vic-Dihalides



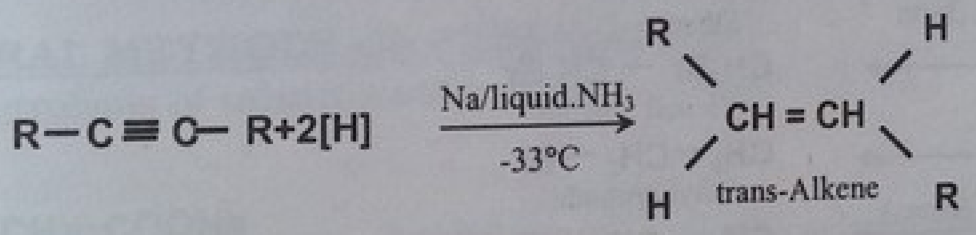
$$R-\underset{X}{\underset{|}{CH}}-\underset{X}{\underset{|}{CH_2}} + Zn \xrightarrow{CH_3OH} \underset{\text{Alkene}}{R-CH=CH_2} + ZnX_2$$

- Partial Hydrogenation of Alkynes



$$R-C\equiv C-R + H_2 \xrightarrow[\text{Quinoline}]{Pd(BaSO_4)}$$

cis-Alkene



$$R-C\equiv C-R + 2[H] \xrightarrow[-33^\circ C]{\text{Na/liquid.}NH_3}$$

trans-Alkene

REACTIONS OF ALKENES (ETHENE)

Reactions	Remarks
	ADDITION REACTIONS
Hydrogenation	▪ Raney Nickel is used as catalyst ▪ Raney Ni is produced after the reaction of Ni-Al alloy with caustic soda ▪ Reaction is exothermic
Addition of HX	▪ Alkenes react with dry gaseous hydrogen halides. ▪ Order of reactivity of halogen acid is HI>HBr>HCl ▪ Reaction mechanism involve carbocation formation ▪ Markownikov's rule implements on asymmetric alkenes.
Sulphonation	Addition of sulphonic group is called sulphonation
Halogenations	▪ Reaction takes place in inert solvent ▪ I_2 does not react with alkene ▪ Reaction mechanism involve carbonium ion formation
Addition of hypohalous acid	▪ Reaction mechanism involve carbonium ion formation ▪ Halohydrins are produced in this reaction ▪ The compound in which X and OH groups are on vicinal C atoms called halo-hydrins

OXIDATION REACTIONS	
Addition of oxygen	▪ Epoxide is produced ▪ Epoxides are used in glycol formation
Ozonolysis	▪ Addition of ozone is called ozonolysis ▪ Ozonide, due to unstability, changes into aldehydes or ketones or both depending upon alkyl group.
Combustion	▪ Burning of alkene is called combustion ▪ Exothermic reaction ▪ Reaction occur in kitchen (stores) and in petrol engine
Hydroxylation	▪ 1% alkaline $KMnO_4$ is also called Baeyer's reagent ▪ $KMnO_4$ colour is discharged during reaction

Polymerization:

In this process small organic molecules (monomers) combine together to form larger molecules known as polymers.

Ethene at 400°C and 100 atm pressure, polymerize to polythene or polyethylene.

$$n\ CH_2=CH_2 \xrightarrow[\text{100 atm pressure traces Of } O_2(0.1\%)]{400^\circ C} -[-CH_2-CH_2-]_n-$$

Polyethylene

A good quality polythene is obtained, when ethane is polymerized in the presence of aluminium triethyl Al $(C_2H_5)_3$ and titanium tetrachloride catalysts $(TiCl_4)$

CHEMICAL REACTIONS OF ETHENE

$$CH_2=CH_2+3O_2 \xrightarrow{\text{Flame}} 2CO_2+2H_2O+\text{heat}$$

$$CH_2=CH_2+H_2 \xrightarrow[\text{100°C,3atm}]{\text{Raney Ni}} CH_3-CH_3$$

Ethane

$$CH_2=CH_2+Br_2 \longrightarrow CH_2Br-CH_2Br$$

Vicinal dihalide

$$CH_2=CH_2+HBr \longrightarrow CH_3-CH_2-Br$$

Ethyl bromide

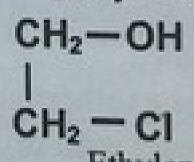
$$\underset{\text{(cold)}}{CH_2=CH_2+H_2SO_4} \xrightarrow{\text{(conc.)}} CH_3-CH_2-OSO_3H$$

Ethyl hydrogen sulphate

$$CH_3-CH_2-HSO_4+H_2O \xrightarrow{100^\circ C} CH_3-CH_2-OH+H_2SO_4$$

Ethyl alcohol

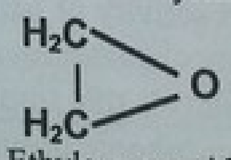
$$CH_2=CH_2+HO\text{–}Cl \xrightarrow{Cl_2+HOH}$$



$$\begin{array}{l} CH_2-OH \\ | \\ CH_2-Cl \end{array}$$

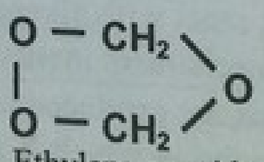
Ethylene chlorohydrin

$$CH_2=CH_2+\tfrac{1}{2}O_2 \xrightarrow[300^\circ C]{Ag_2O}$$

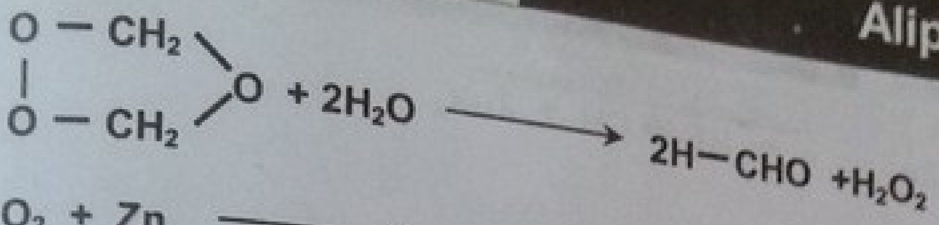


Ethylene epoxide

$$CH_2=CH_2+O_3 \xrightarrow{\text{Ether}}$$

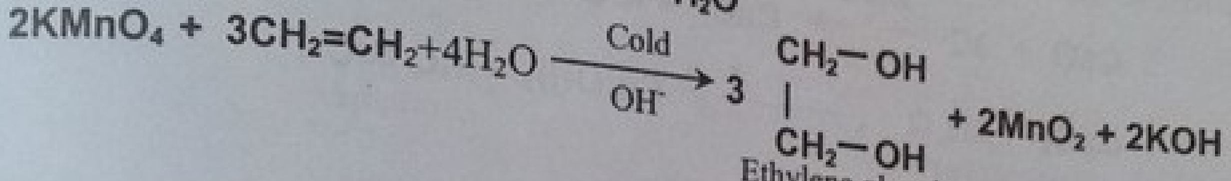


Ethylene ozonide



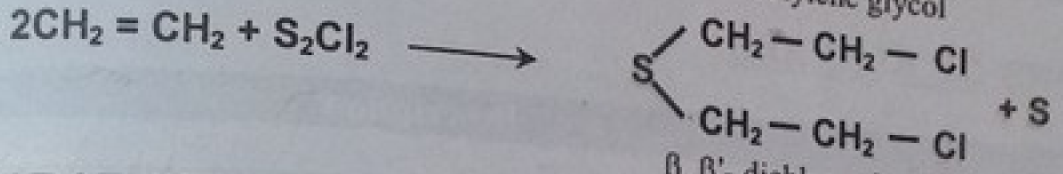
$$\text{(ozonide)} + 2H_2O \longrightarrow 2H{-}CHO + H_2O_2$$

$$H_2O_2 + Zn \longrightarrow ZnO + H_2O$$



$$2KMnO_4 + 3CH_2{=}CH_2 + 4H_2O \xrightarrow[OH^-]{Cold} 3\begin{array}{c}CH_2{-}OH\\ |\\ CH_2{-}OH\end{array} + 2MnO_2 + 2KOH$$

Ethylene glycol



$$2CH_2 = CH_2 + S_2Cl_2 \longrightarrow S(CH_2{-}CH_2{-}Cl)_2 + S$$

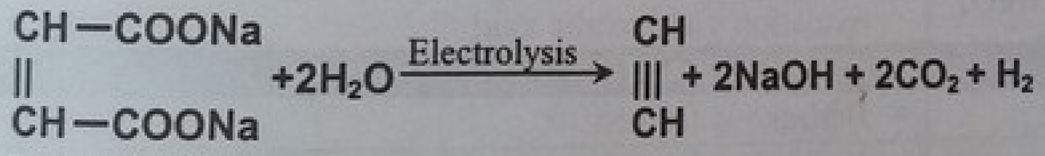
β, β'- dichloroethyl sulphide
(Mustard gas)

PREPARATION OF ALKYNES

Methods	Description
Dehydrohalogenation of dihalides	▪ Removal of HX is called dehydrohalogenation ▪ Reaction completes in two steps. ▪ Normally alcoholic KOH is used
Dehalogenation of tetrahalides	▪ Removal of halogen from a a vicinal haloalkane is called dehalogenation ▪ Salts of Mg can be used instead of Zn
Electrolysis of dicarboxylic acid salts	▪ Salt of unsaturated dicarboxylic acid are subjected to electrolysis producing alkynes
From CaC_2	▪ On industrial scale, it is used to produce ethyne.

GENERAL METHODS OF PREPARATION

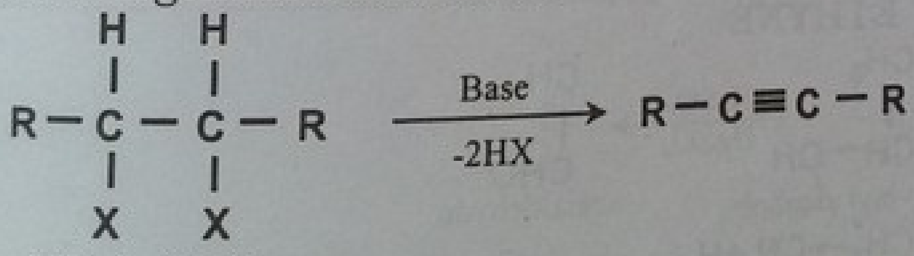
- Electrolysis of unsaturated salts of dicarboxylic acids



$$\begin{array}{c}CH{-}COONa\\ \|\\ CH{-}COONa\end{array} + 2H_2O \xrightarrow{Electrolysis} \begin{array}{c}CH\\ |||\\ CH\end{array} + 2NaOH + 2CO_2 + H_2$$

Sodium maleate

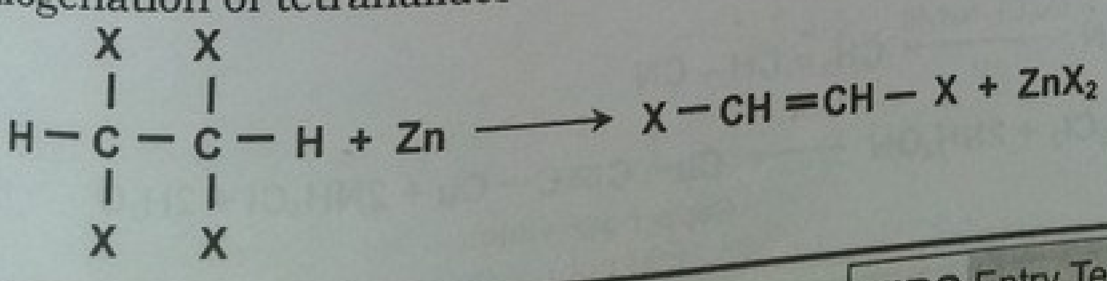
- Dehydrohalogenation of dihalides



$$R{-}\underset{X}{\overset{H}{C}}{-}\underset{X}{\overset{H}{C}}{-}R \xrightarrow[-2HX]{Base} R{-}C{\equiv}C{-}R$$

Vicinal dihalide

- Dehalogenation of tetrahalides



$$H{-}\underset{X}{\overset{X}{C}}{-}\underset{X}{\overset{X}{C}}{-}H + Zn \longrightarrow X{-}CH{=}CH{-}X + ZnX_2$$

$X-CH=CH-X + Zn \longrightarrow HC\equiv CH + ZnX_2$

- Industrial Method

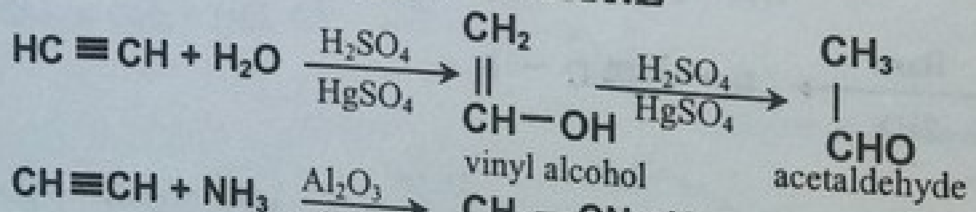
$CaO + 3C \xrightarrow{2000°C} CaC_2 + CO$

$\underset{\text{Calcium carbide}}{CaC_2 + 2H_2O} \longrightarrow Ca(OH)_2 + \underset{\text{ethyne}}{HC\equiv CH}$

CHEMICAL REACTIONS OF ALKYNES

Reaction	Description
ADDITION REACTIONS	
Hydrogenation	▪ Addition of hydrogen is called hydrogenation ▪ Pt and Pd can be used as catalyst instead of Ni
Halogenation	▪ Addition of halogen is halogenation ▪ CCl_4 act as catalyst ▪ Iodine reacts more slowly than other halogens
Addition of halogen acid	▪ Markownikov's rule is applicable in the 1st step of reaction ▪ Reaction completes in two steps
Addition of water	▪ Vinyl alcohol is formed at first, which is unstable and changes into acetaldehyde
Addition of ammonia and Hydrogen cyanide	▪ The addition products are alkyl nitrile & acrylonitrile respectively.
OXIDATION REACTIONS	
In air	▪ Reaction is exothermic ▪ The burning flame is called oxyacetylene flame that is used in welding purpose.
With oxidizing agent like $KMnO_4$	▪ $KMnO_4$ loses its colour during the reaction and glyoxal on oxidation yield oxalic acid
POLYMERIZATION	
In Cu tube at 300°C	▪ Benzene is formed
With Cu_2Cl_2/NH_4Cl as catalyst	▪ Vinyl acetylene is formed ▪ Vinyl acetylene → chloroprene HCl → neoprene (synthetic rubber)

CHEMICAL REACTIONS OF ETHYNE



$HC\equiv CH + H_2O \xrightarrow[HgSO_4]{H_2SO_4} \underset{\text{vinyl alcohol}}{CH_2=CH-OH} \xrightarrow[HgSO_4]{H_2SO_4} \underset{\text{acetaldehyde}}{CH_3-CHO}$

$CH\equiv CH + NH_3 \xrightarrow[300°C]{Al_2O_3} CH_3-CN + H_2$

$CH\equiv CH + HCN \xrightarrow[\Delta H]{Cu_2Cl_2/NH_4Cl} CH_3=CH-CN$

$CH\equiv CH + Cu_2Cl_2 + 2NH_4OH \longrightarrow \underset{\substack{\text{Copper acetylide}\\\text{(red ppt.)}}}{Cu-C\equiv C-Cu} + 2NH_4Cl + 2H_2O$

$CH\equiv CH + 2AgNO_3 + 2NH_4OH \longrightarrow Ag-C\equiv C-Ag + 2NH_4NO_3 + 2H_2O$

Silver acetylide
(white ppt.)

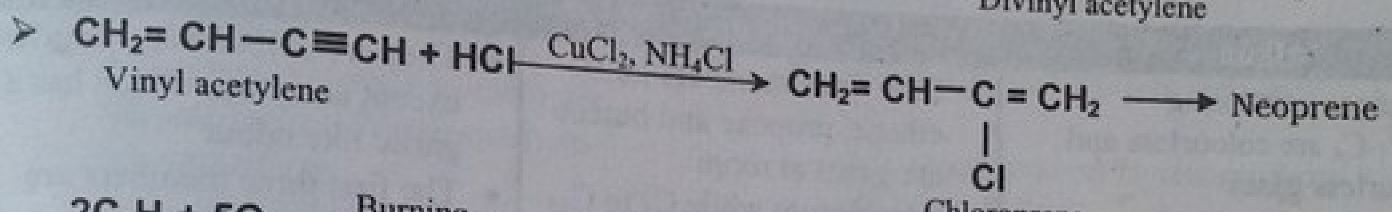
$Ag-C\equiv C-Ag + dil.H_2SO_4 \longrightarrow CH\equiv CH + Ag_2SO_4$

- $2CH\equiv CH \xrightarrow[NH_4Cl]{Cu_2Cl_2} CH_2=CH-C\equiv CH$

  Vinyl acetylene

➢ $CH_2=CH-C\equiv CH + CH\equiv CH \xrightarrow{CuCl_2,\ NH_4Cl} CH_2=CH-C\equiv C-CH=CH_2$

Divinyl acetylene



➢ $\underset{\text{Vinyl acetylene}}{CH_2=CH-C\equiv CH} + HCl \xrightarrow{CuCl_2,\ NH_4Cl} CH_2=CH-\underset{\displaystyle Cl}{\underset{|}{C}}=CH_2 \longrightarrow \text{Neoprene}$

Chloroprene

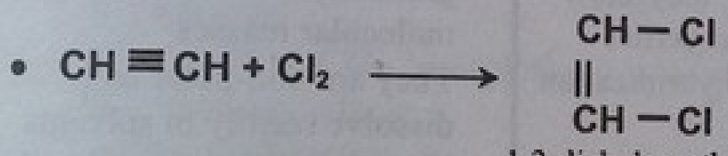
$2C_2H_2 + 5O_2 \xrightarrow{\text{Burning}} 4CO_2 + 2H_2O + \text{heat}$

- $CH\equiv CH + H_2 \xrightarrow[\text{heat}]{Ni} CH_2=CH_2$

  Ethylene

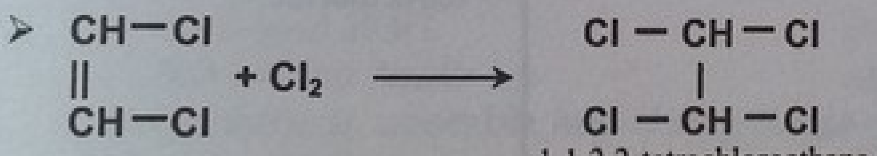
➢ $CH_2=CH_2 + H_2 \xrightarrow[\text{heat}]{Ni} CH_3-CH_3$

Ethane



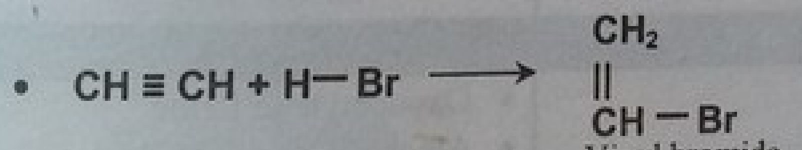
- $CH\equiv CH + Cl_2 \longrightarrow \begin{array}{c} CH-Cl \\ \| \\ CH-Cl \end{array}$

  1,2-dicholoroethene



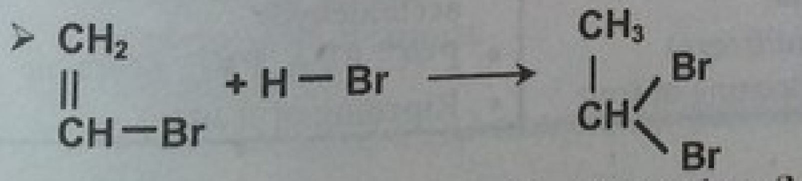
➢ $\begin{array}{c} CH-Cl \\ \| \\ CH-Cl \end{array} + Cl_2 \longrightarrow \begin{array}{c} Cl-CH-Cl \\ | \\ Cl-CH-Cl \end{array}$

1,1,2,2-tetrachloroethane



- $CH\equiv CH + H-Br \longrightarrow \begin{array}{c} CH_2 \\ \| \\ CH-Br \end{array}$

  Vinyl bromide

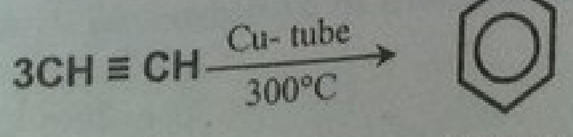


➢ $\begin{array}{c} CH_2 \\ \| \\ CH-Br \end{array} + H-Br \longrightarrow \begin{array}{c} CH_3 \\ | \\ CH\!\begin{array}{l} Br \\ Br \end{array} \end{array}$

1,1-dibromoethane (Markownikov's rule)
ethylidine dibromide

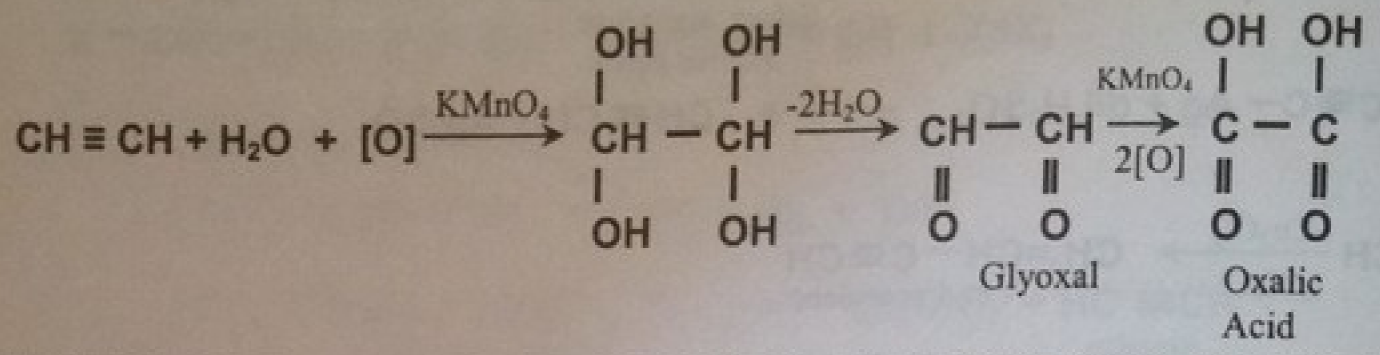
$CH\equiv CH + Na \xrightarrow{210°C} NaC\equiv CNa + H_2$

di Sodium Acetylide



$3CH\equiv CH \xrightarrow[300°C]{\text{Cu- tube}}$

Benzene



$$CH\equiv CH + H_2O + [O] \xrightarrow{KMnO_4} \underset{OH}{\overset{OH}{CH}}-\underset{OH}{\overset{OH}{CH}} \xrightarrow{-2H_2O} \underset{O}{\underset{\|}{CH}}-\underset{O}{\underset{\|}{CH}} \xrightarrow[2[O]]{KMnO_4} \underset{O}{\underset{\|}{\overset{OH}{C}}}-\underset{O}{\underset{\|}{\overset{OH}{C}}}$$

PHYSICAL PROPERTIES OF ALKANES, ALKENES AND ALKYNES

Alkanes	Alkenes	Alkynes
• Alkanes containing →C_1-C_4 are colourless and odourless gases →C_5-C_{17} are colourless and odourless liquids →C_{18} onwards are colourless and odourless waxy solids • Being non-polar, they are insoluble in water but soluble in non-polar solvents • Their physical constants Boiling point, Melting Point, density etc) increase with the increase in number of carbon atoms • Solubility decreases with increase in molecular mass. • The boiling points of alkanes having branched chain structures are lower than their isomeric normal chain alkanes	• First three members i.e ethene, propene and butene are gases at room temperature while C_5 to C_{15} are liquids and the higher members are solids • They are insoluble in water but soluble in alcohol • They have characteristic smell and burn with luminous flame • Unlike alkanes, they show weakly polar properties because of sp^2 hybridization	• They are colourless, odourless, except acetylene which has a garlic like odour • The first three members are gases (ethyne, propyne, butyne) at room temperature • The next eight members (C_5-C_{12}) are liquids and higher members are solids • The melting points, boiling points and densities increase gradually with the increase in molecular masses • They are non-polar and dissolve readily in solvents like ether, benzene and carbon tetrachloride
	USES	
• Illuminating gas cylinder • $CHCl_3$, CCl_4, CH_3OH, HCOH, HCN • Carbon black, printing ink, automobile tyres	Polyethylene • Anesthesia • Mustard gas • Glycols (antifreeze) Artificial ripening of fruit	• Oxyacetylene flame • Alcohols, acetic acids, acetaldehyde • PVC, PVA, PVE, neoprene • Ripening of fruits

KIPS

Chapter 8

Aliphatic Hydrocarbons

PRACTICE EXERCISE

20 mins
Time Yourself

1. Alkanes containing a methyl group on main chain at 2nd carbon are called
   (a) iso-alkane
   (b) normal-alkane
   (c) neo-alkane
   (d) branched-alkane
2. When one hydrogen atom of alkane is removed, then it is called
   (a) alkene
   (b) alkyl
   (c) aldehyde
   (d) saturated hydrocarbon
3. Alkanes are also known as
   (a) saturated hydrocarbon
   (b) unsaturated hydrocarbon
   (c) paraffins
   (d) both a & c
4. Sabatier Sendern's reaction involve __________ in presence of Ni
   (a) alkene & H_2
   (b) alkene & O_2
   (c) alkene & N_2
   (d) alkyne & Cl_2
5. Hydrogenolysis results in the formation of
   (a) alkane
   (b) alkene
   (c) alkyne
   (d) aldehydes
6. Clemmensen's reduction involves the reduction of
   (a) ketone
   (b) aldehyde
   (c) alkane
   (d) all of the above
7. Removal of CO_2 is called
   (a) carboxylation
   (b) decarboxylation
   (c) esterification
   (d) hydroxylation
8. Soda lime is a mixture of
   (a) CaO and KOH
   (b) CaO and NaOH
   (c) NaOH and Na_2O
   (d) Na_2O and KOH
9. Molozonide is unstable and changes into ozonide on
   (a) reduction
   (b) oxidation
   (c) hydrolysis
   (d) rearrangement
10. Dehalogenation of ethyl tetrahalide will give
    (a) ethene
    (b) ethyne
    (c) ethyl halide
    (d) all of the above are possible
11. R-Mg-Br is called
    (a) Grignard reagent
    (b) Metallic alkyl halide
    (c) Both a & b
    (d) Alkyl halide
12. Upto __________ C atoms, alkanes are gases
    (a) 2
    (b) 3
    (c) 4
    (d) 6
13. Which of the following is the most reactive
    (a) ethane
    (b) ethyne
    (c) ethene
    (d) benzene
14. Incomplete oxidation of methane in the limited supply of air forms.
    (a) CO_2 and H_2O
    (b) CH_3OH
    (c) $CO + H_2 + C$
    (d) $CO + H_2O + C$

15. Introduction of nitro group in a molecule is called
(a) nitration
(b) halogenation
(c) sulphonation
(d) amination

16. Order of ease of halogenation in alkane is
(a) $I_2>Cl_2>Br_2>F_2$
(b) $F_2>Cl_2>I_2>Br_2$
(c) $F_2>Cl_2>Br_2>I_2$
(d) $Cl_2>F_2>Br_2>I_2$

17. The gas used in manufacturing of urea fertilizer
(a) C_2H_6
(b) C_2H_4
(c) C_2H_2
(d) CH_4

18. General formula of alkyne is
(a) C_nH_{2n+2}
(b) C_nH_{2n-2}
(c) C_nH_{2n}
(d) C_nH_{2n+1}

19. Which of the following will be acidic
(a) propyne
(b) 1-butyne
(c) ethyne
(d) all of the above

20. Removal of halogen and hydrogen atom is
(a) halogenation
(b) dehalogenation
(c) dehydrohalogenation
(d) hydrohalogenation

21. Alkenes are produced from dehalogenation of
(a) dihalo alkane
(b) trihalo alkane
(c) vicinal dihalo alkane
(d) vicinal trihalo alkane

22. Reactivity due to pi- electrons is present in
(a) alkane
(b) alkene
(c) alkyne
(d) both b & c

23. In unsaturated hydro carbons, π-electrons favour
(a) less reactivity
(b) addition reactions
(c) substitution reactions
(d) none

24. Raney nickel is prepared from ——— by treating with caustic soda
(a) Ni-Cu alloy
(b) Ni-Fe alloy
(c) Ni-Al alloy
(d) Ni-Mg alloy

25. Which one is Chloroform
(a) CH_2Cl_2
(b) CH_3Cl
(c) $CHCl_3$
(d) CCl_4

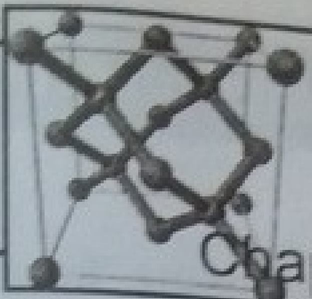
26. Vinylacetylene combines with HCl to form
(a) polyacetylene
(b) benzene
(c) chloroprene
(d) divinyl acetylene

27. β,β̄-dichloroethyl sulphide is commonly known as
(a) laughing gas
(b) bio-gas
(c) mustard gas
(d) phosgene gas

28. Which is used for artificial ripening of fruit?
(a) ethane
(b) ethene
(c) ethyne
(d) methane

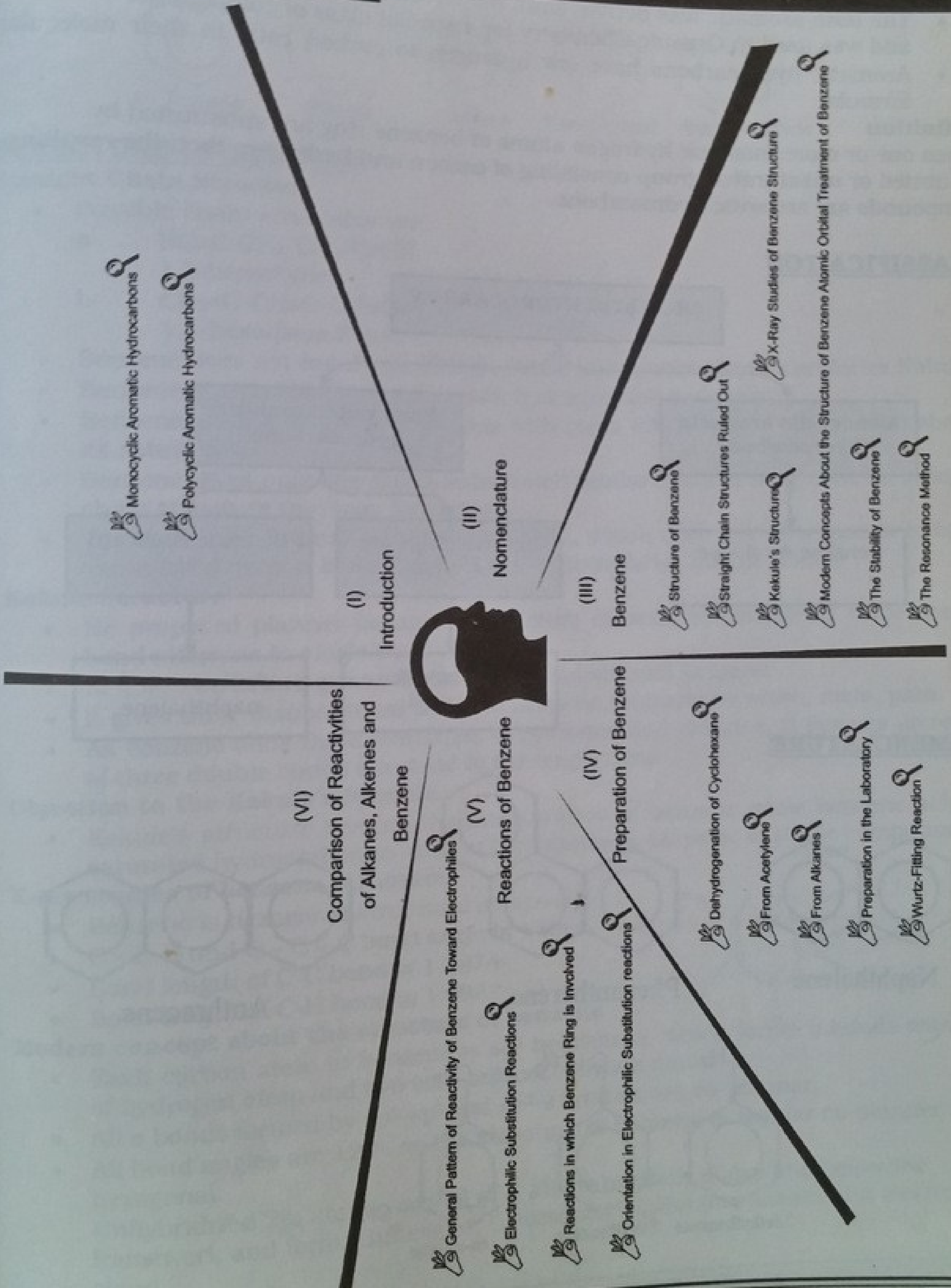
29. Preparation of vegetable ghee involves
(a) halogenation
(b) hydroxylation
(c) hydrogenation
(d) hydration

30. Which is methyl cyanide
(a) CH_3NH_2
(b) CH_3NO_2
(c) CH_3CN
(d) $CH_2=CH-CN$



Chapter 9

AROMATIC HYDROCARBONS


(I)
Introduction
Monocyclic Aromatic Hydrocarbons
Polycyclic Aromatic Hydrocarbons
(II)
Nomenclature
(III)
Benzene
Structure of Benzene
Straight Chain Structures Ruled Out
X-Ray Studies of Benzene Structure
Kekule's Structure
Modern Concepts About the Structure of Benzene Atomic Orbital Treatment of Benzene
The Stability of Benzene
The Resonance Method
(IV)
Preparation of Benzene
Dehydrogenation of Cyclohexane
From Acetylene
From Alkanes
Preparation in the Laboratory
Wurtz-Fitting Reaction
(V)
Reactions of Benzene
General Pattern of Reactivity of Benzene Toward Electrophiles
Electrophilic Substitution Reactions
Reactions in which Benzene Ring is Involved
Orientation in Electrophilic Substitution reactions
(VI)
Comparison of Reactivities of Alkanes, Alkenes and Benzene

Chapter 9

Aromatic Hydrocarbons

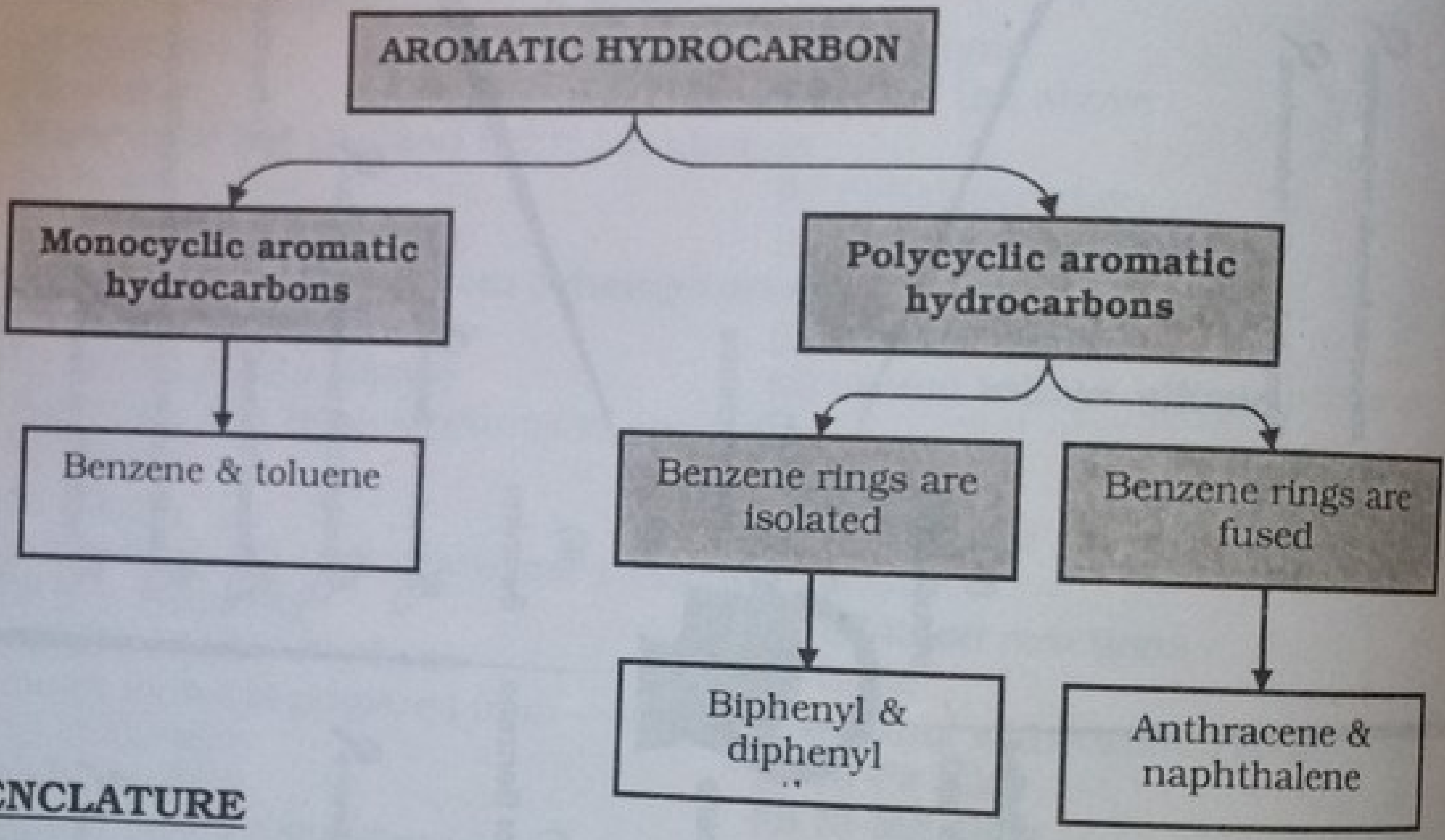
INTRODUCTION

- The term aromatic was derived from the Greek word 'aroma' meaning "fragrant" and was used in Organic Chemistry for a special class of compounds.
- Aromatic hydrocarbons have low hydrogen to carbon ratio in their molecular formula.

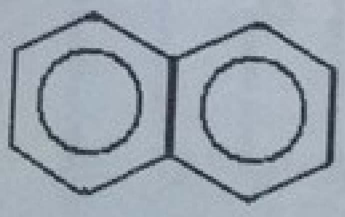
Definition

When one or more than one hydrogen atoms of benzene ring are substituted by saturated or unsaturated group consisting of carbon and hydrogen, then the resulting compounds are aromatic hydrocarbons.

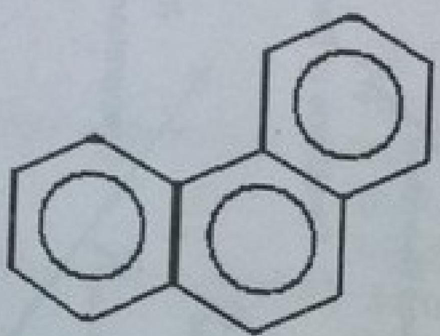
CLASSIFICAITON



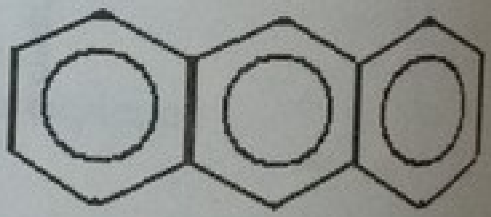
NOMENCLATURE



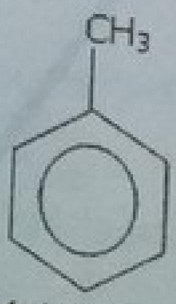
Naphthalene



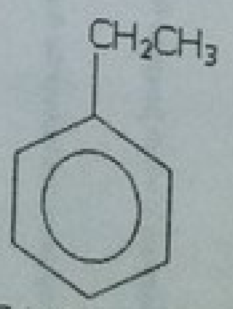
Phenantharene



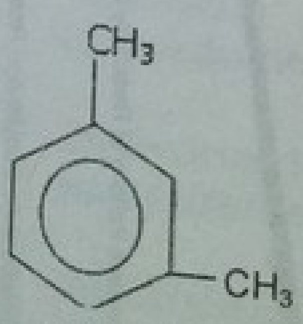
Anthracene



Methylbenzene



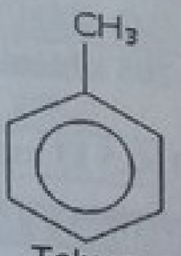
Ethylbenzene



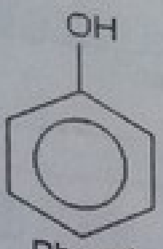
m-xylene

Chapter 9

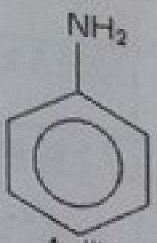
Aromatic Hydrocarbons



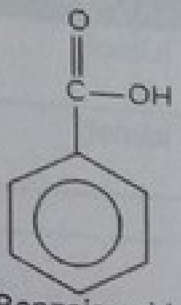
Toluene



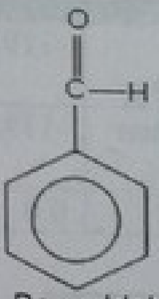
Phenol



Aniline



Benzoic acid



Benzaldehyde

STRUCTURE OF BENZENE

Straight Chain Structure

- Possible chain structures are:
  - a- HC≡C-CH_2-CH_2-C≡CH
    1,5-hexadiyne
  - b- CH_2=C-CH≡C-CH=CH_2
    1,5-hexadiene,3-yne
- Benzene does not decolorize $KMnO_4$, while alkene and alkyne decolorize $KMnO_4$.
- Benzene gives addition reaction with hydrogen and halogens.
- Benzene gives substitution reaction with conc. HNO_3, conc. H_2SO_4 which shows its saturation.
- Benzene gives only one mono substituted product, which is against its straight chain structure that may form three.
- The molecular formula of benzene is C_6H_6, which does not corresponds to open chain hydrocarbon like alkane (C_6H_{14}), alkene C_6H_{12}, alkyne (C_6H_{10})

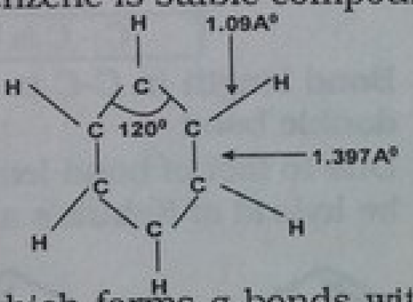
Kekule Structure

- He proposed planner hexagonal structure of benzene containing three double bond alternate to single bond
- Kekule's structure gives only one mono substituted benzene
- It gives three disubstituted benzene isomeric products i-e ortho, meta, para.
- As benzene adds three molecules of hydrogen and chlorine, it favours presence of three double bonds alternate to the single bond

Objection to the Kekule's formula

- Kekule's structure favours the unsaturation of benzene while benzene acts as saturated hydrocarbon in most of the reactions. Benzene is stable compound.

X-ray studies of benzene structure



- Benzene is hexagonal structural compound
- C - C-H and C – C – C bond angle is 120°
- Bond length of C-C bond is 1.397A°
- Bond length of C-H bond is 1.09A°

Modern concept about the structure of benzene

- Each carbon atom in benzene is sp^2 hybridized, which forms σ bonds with one of hydrogen atom and two with adjacent carbon atoms.
- All σ bonds formed by sp^2-sp^2 and sp^2-s orbitals are co-planner.
- All bond angles are 120°, so the structure of benzene is regular co-planner hexagonal.
  Unhybridized $2p_z$ atomic orbital of C atoms overlaps above and below the framework and forms diffused or delocalized continuous sheath of π electron cloud.

	Cyclohexene	1.3 Cyclohexadiene	1,3,5cyclohexatriene
Expected hydrogenation energy	-119.5 kJmol^{-1}	-239 kJ mol^{-1}	-358.5 kJ mol^{-1}
Actual hydrogenation energy	-119.5 kJmol^{-1}	-231.5 kJ mol^{-1}	-208 kJ mol^{-1}
Resonance energy	0.0	7.5 kJ mol^{-1}	150.5 kJ mol^{-1}

The stability of benzene

- The stability of benzene is due to the Extensive delocalization of electron cloud
- The delocalized electrons increases the stability of benzene
- Heat of hydrogenation of cyclohexane and 1,3-cyclohexadiene is -119.5KJ/mole and -231.5 KJ/mole respectively
- Due to the phenomenon of resonance and resonance energy, the heat of hydrogenation of benzene is lesser (-208KJ/mole) than that of 1, 3, 5 – cyclohexatriene.

Delocalized Electrons

When the shared electrons are attracted by more than two nuclei, such electrons are called delocalized electrons.

THE RESONANCE METHOD

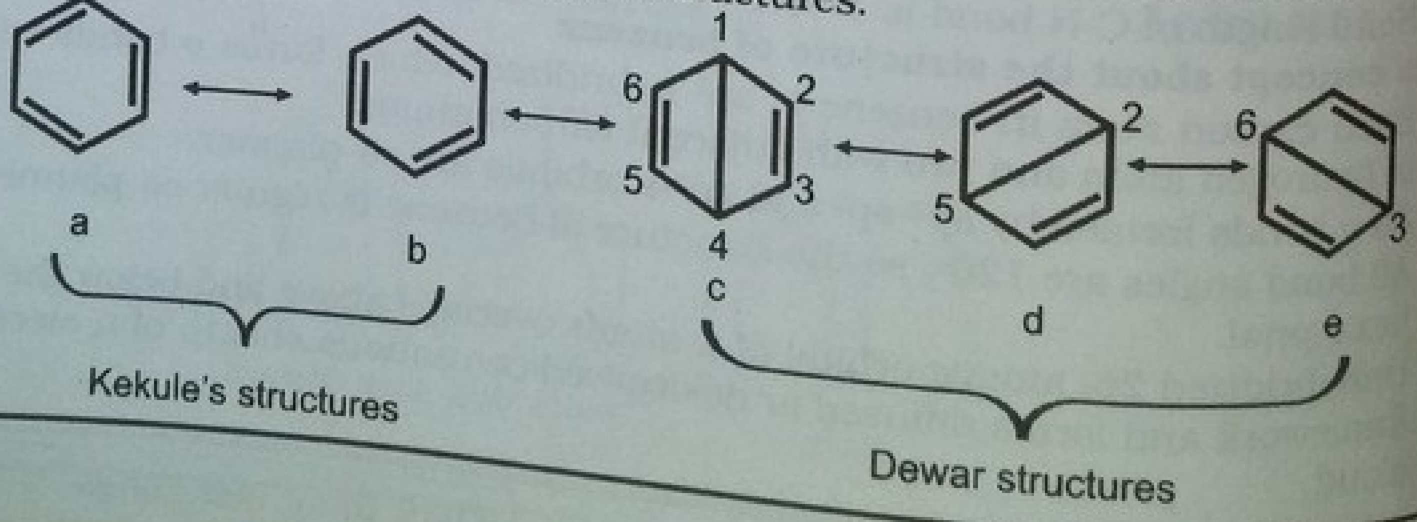
Resonance

The possibility of different pairing schemes of valence electrons of atoms is called resonance and the different structures thus arranged are called Resonance structures.

- Different Lewis structures are called resonance contributing structures or canonical forms.
- The resonance structures are represented by (↔) double headed arrow
- Dewar is the scientist, who gave the concepts of para bonds in structure of benzene. But his structure contributes very little in prediction of actual structure of benzene
- Kekule's structure of benzene (alternate double bonds in planner hexagonal ring) contributed more in prediction of actual structure of benzene.
- Bond lengths in hydrocarbon are as under:

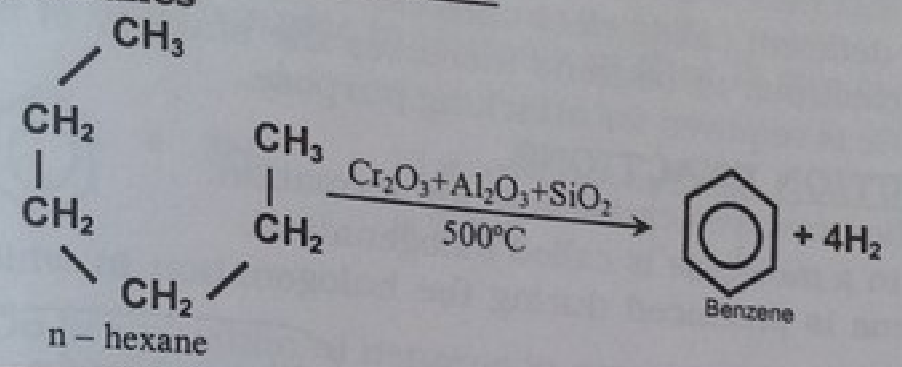
Nature of bond	Bond length
C – C	1.54A°
C = C	1.34A°
C ≡ C	120A°
C – C in benzene	1.397A°

- Bond length in C-C in benzene (1.397A°) shows that it is in between single and double bond
- Due to fact of bond length, it was proposed that actual structure of benzene will be hybrid of Kekule's and Dewar's structures.

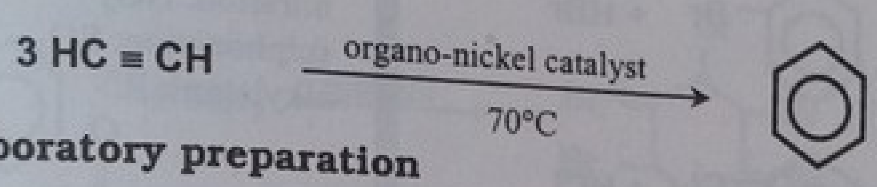


PREPARATION OF BENZENE

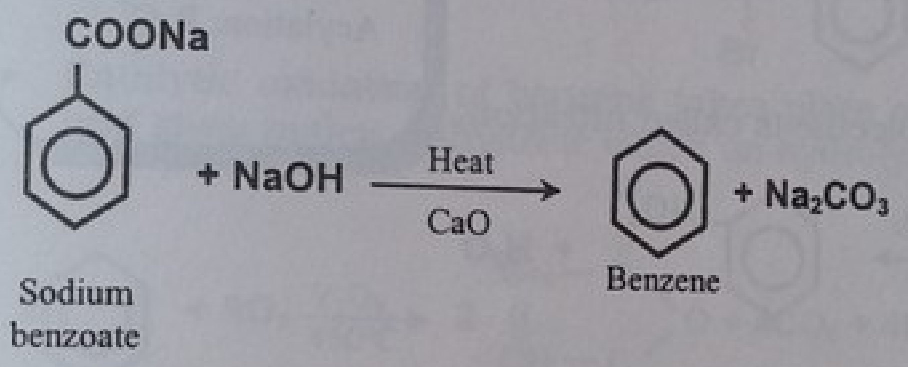
1. From alkanes

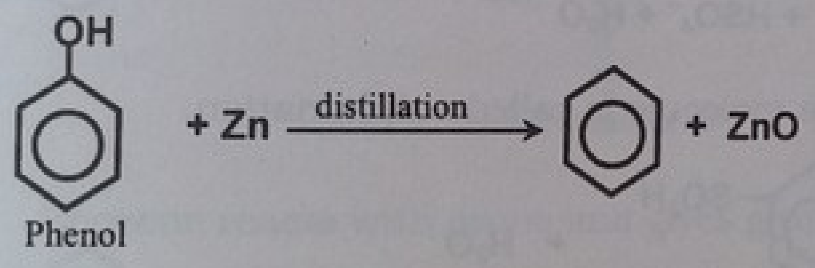


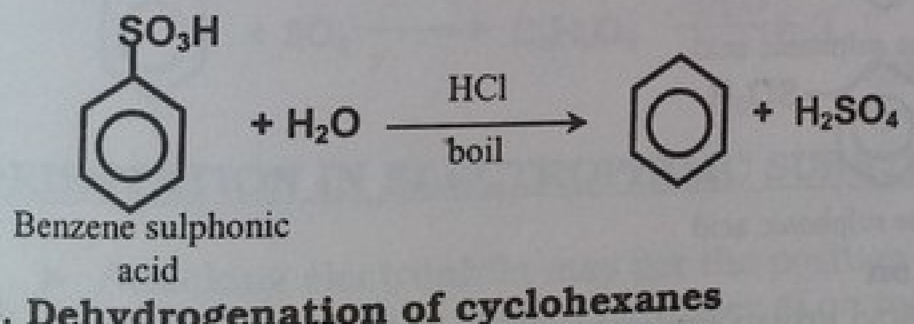
2. From acetylene



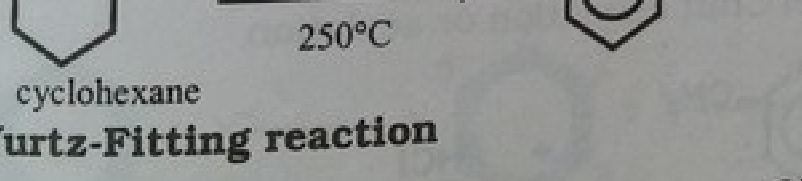
3. Laboratory preparation



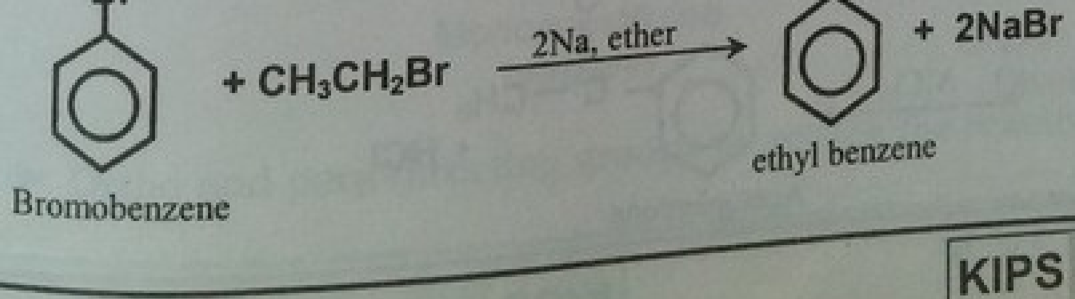




4. Dehydrogenation of cyclohexanes



5. Wurtz-Fitting reaction



REACTIONS OF BENZENE

Electrophiles

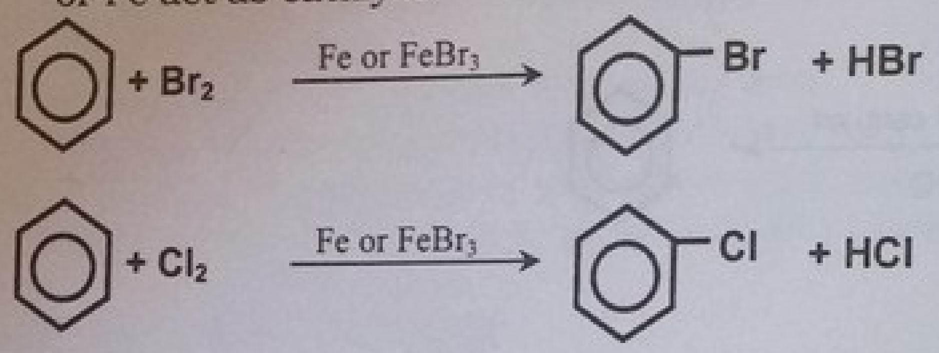
The species which are electron deficient called electrophiles.

- Presence of delocalized electrons in benzene increases the stability of benzene. So very strong electrophile is required for attacking purpose.

ELECTROPHILIC SUBSTITUTION REACTIONS

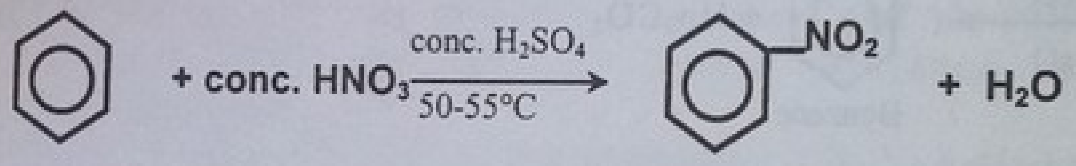
Electrophilic substitution reaction involves carbonium ion formation.

- Introduction of halogen in a molecule is called halogenation.
- Mono substituted benzene is produced during the halogenation in which FeX or Fe act as catalyst.



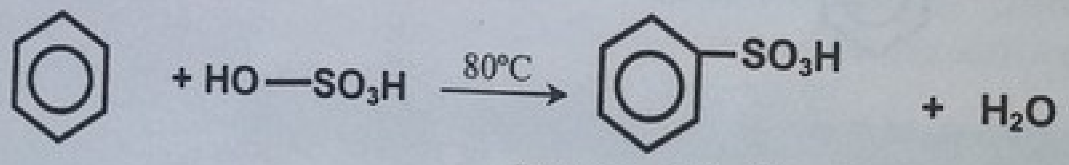
Electrophiles for
nitration: NO_2^+
sulphonation: SO_3
alkylation: R^+
Acylation: $R\text{-}\overset{\overset{O}{\|}}{C}^+$

- Introduction of $-NO_2$ in a molecule is called nitration.

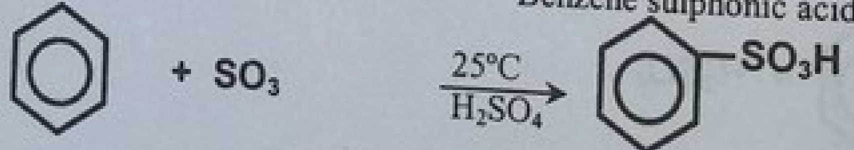


$$HNO_3 + H_2SO_4 \rightleftharpoons NO_2^+ + HSO_4^- + H_2O$$

- Introduction of HSO_3^+ group in a molecule is called sulphonation.



Benzene sulphonic acid

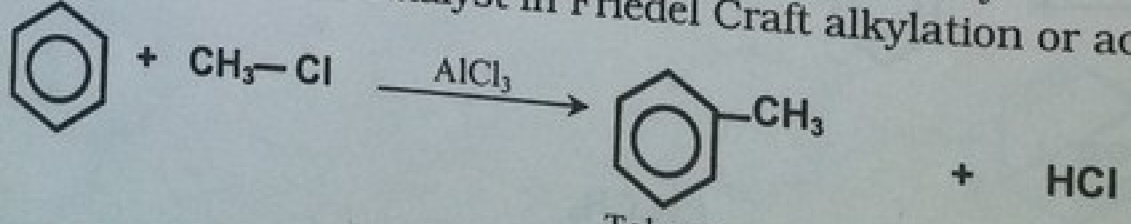


Benzene sulphonic acid

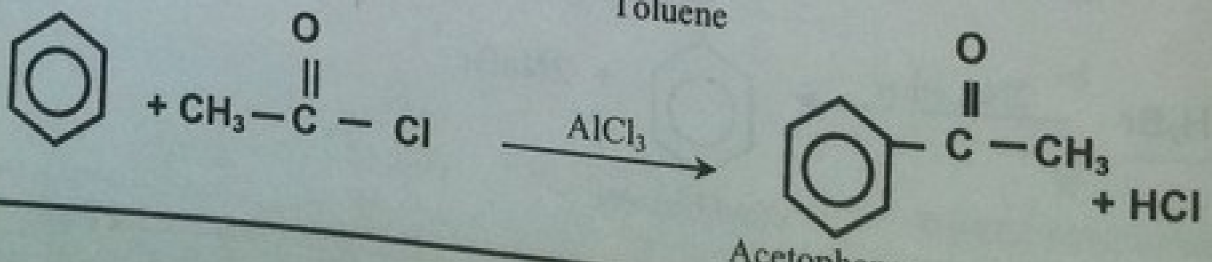
Friedel Craft alkylation and acylation

The reaction in which alkyl group or acyl group replaces the hydrogen of benzene is called Friedel Craft alkylation and acylation respectively.

- $AlCl_3$ is used as catalyst in Friedel Craft alkylation or acylation



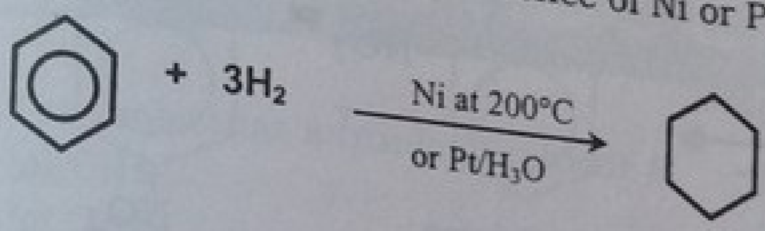
Toluene



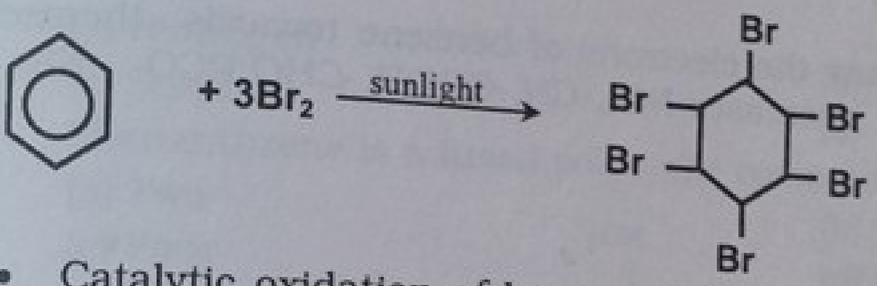
Acetophenone

REACTIONS IN WHICH BENZENE RING IS INVOLVED

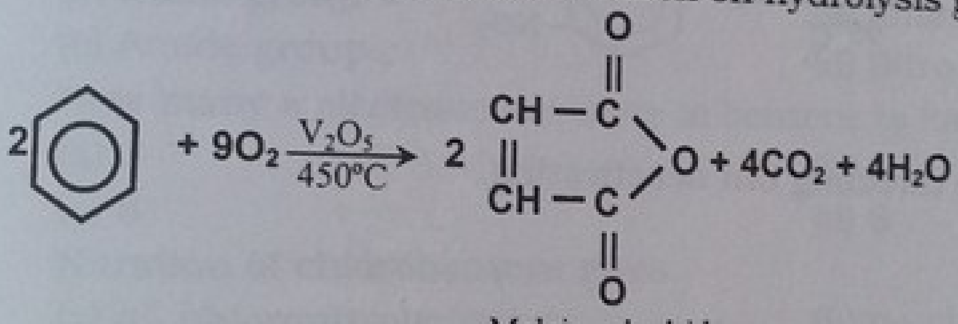
Addition of H_2 in benzene in presence of Ni or Pt give cyclohexane



- On bromination of benzene in presence of sunlight, hexabromo cyclohexane is produced

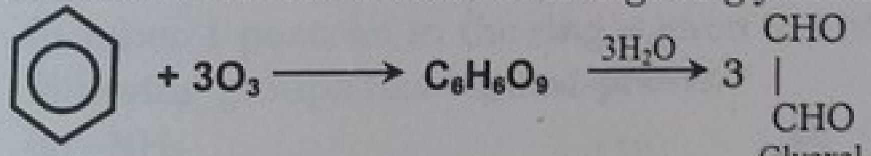


- Catalytic oxidation of benzene takes place on heating in the presence of V_2O_5 and gives maleic anhydride which on hydrolysis gives maleic acid



Maleic anhydride

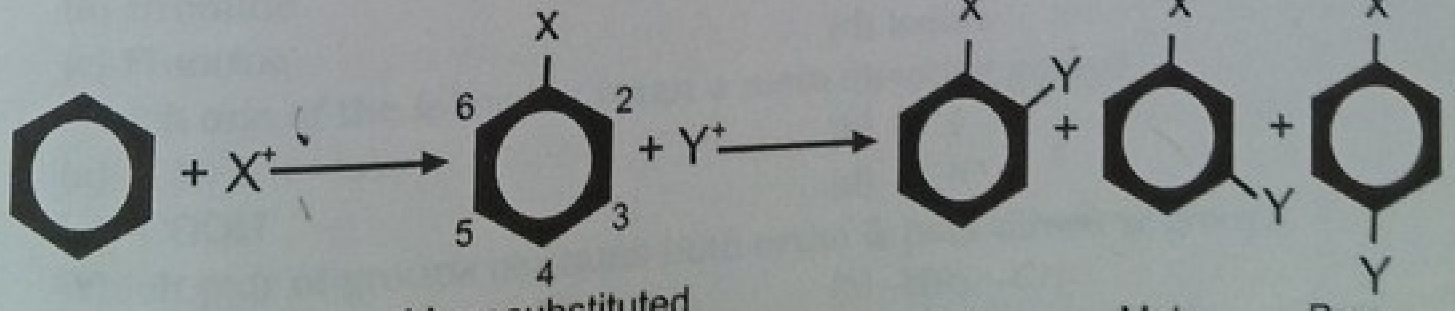
- Benzene reacts with ozone and gives glyoxal through benzene triozonide.



Glyoxal

ORIENTATION IN ELECTROPHILIC SUBSTITUTION REACTIONS

- ▶ Attacking electrophile may get the position on ortho (C number 2 or 6), meta (C number 3 or 5) or para (C number 4) on monosubstituted benzene.

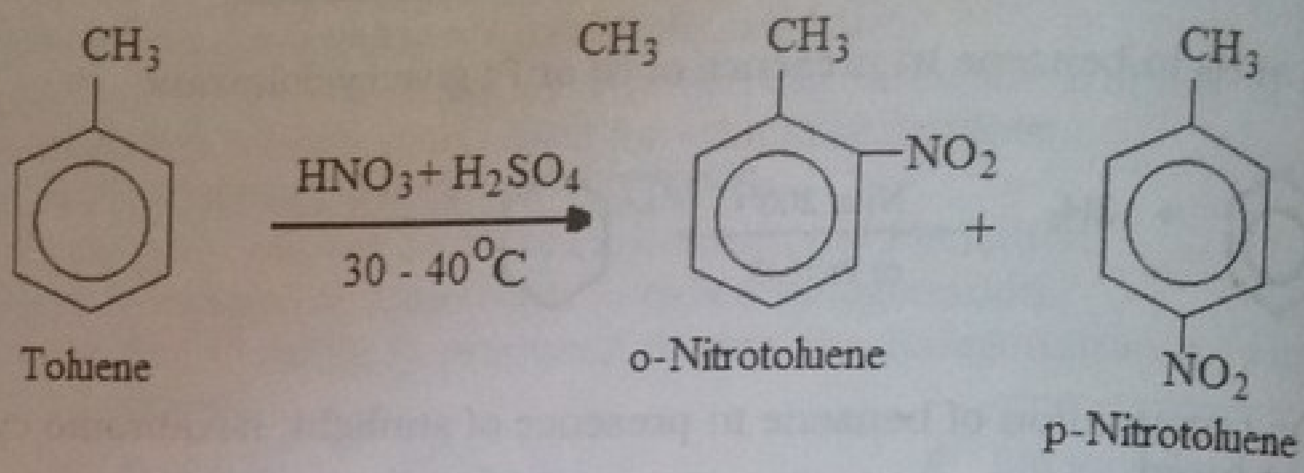


Monosubstituted benzene

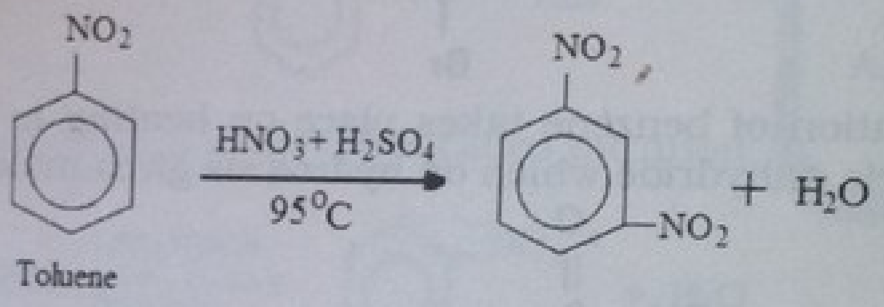
Ortho Meta Para
Disubstituted benzenes

- ▶ Ortho and para directing groups increases the reactivity of benzene.

- $-CH_3$, $-N(CH_3)_2$, $-NH_2$, $-OH$, $-OCH_3$, $-Cl$, $-Br$, $-I$ are ortho and para directing groups



- Meta directing groups withdraw the electrons of benzene towards themselves so the reactivity of benzene decreases-NO_2,-CN,-COOH,-CHO,RCO- $-NR_3$ are meta directing groups.



- Halo group is ortho-para directing but deactivating.

PRACTICE EXERCISE

30 mins
Time Yourself

The molecular formula of toluene is

(a) C_7H_7
(b) C_7H_8
(c) C_8H_8
(d) C_8H_7

In benzene sulphonic acid, the sulphonic group is attached with benzene ring through

(a) Hydrogen
(b) Oxygen
(c) Sulphur
(d) -OH

Phenanthrene is a fused polycyclic compound contains_______ benzene rings

(a) Two
(b) Three
(c) Four
(d) Five

Aniline is a derivative of benzene which contains

(a) Imino group
(b) Amino group
(c) Amide group
(d) Nitro group

How many π electrons are there in benzene to form delocalized electronic cloud.

(a) 3
(b) 4
(c) 6
(d) 8

Nitration of chlorobenzene gives.

(a) o - chloronitrobenzene
(b) p - chloronitrobenzene
(c) m – chloronitrobenzene
(d) a & b

When two or more different substituents are attached with a benzene ring, the number 1 position in the ring is given to a high priority group. Which one of the following groups has highest-priority?

(a) $-NH_2$
(b) $-CHO$
(c) $-COOH$
(d) $-CN$

When benzene is substituted by halogens only, which one of the following halogens is given the number one position in the ring while writing the name of compound?

(a) Bromine
(b) Chlorine
(c) Fluorine
(d) Iodine

Which one of the following is not a meta directing group?

(a) $-CN$
(b) $-OH$
(c) $-COOH$
(d) $-CHO$

0. Which pair of groups contains both ortho & para directing groups.

(a) $-OH, -RCO$
(b) $-NR_3, -CN$
(c) $-OCH_3, -CHO$
(d) $-N(CH_3)_2, -NH_2$

11. Michael Faraday discovered benzene in the gas which was produced by destructive distillation of vegetable oil that is done in
(a) The presence of Oxygen
(b) The presence of Hydrogen
(c) The absence of Oxygen
(d) The presence of excessive Oxygen

12. By which method, the molecular mass of benzene was determined as 78.108?
(a) Specific gravity method
(b) Vapour density method
(c) X-ray diffraction method
(d) Distillation method

13. How many moles of H_2 are added up when benzene is heated with hydrogen in the presence of platinum?
(a) Two
(b) Three
(c) Four
(d) Six

14. Chlorination of toluene in the presence of sunlight produces
(a) Benzyl chloride
(b) o - chlorotoluene
(c) p – chlorotoluene
(d) benzoic acid

15. The heat of hydrogenation of cyclohexene is
(a) -239 kJ mol^{-1}
(b) -208 kJ mol^{-1}
(c) –119.5 KJ/mole
(d) –119.5 Kcal/mole

16. The resonance energy of benzene is
(a) 150.5 KJ/mol
(b) 250.5 KJ/mol
(c) 150.5 Cal/mol
(d) 250.5 Cal/mol

17. The different resonance structures are represented by
(a) $\longleftrightarrow$
(b) $\leftharpoondown$
(c) $\rightharpoonup$
(d) $\cong$

18. What catalyst is employed when benzene is prepared from acetylene at 70°C?
(a) $Cr_2O_3 + A\ell_2O_3 + SiO_2$
(b) Raney nickel
(c) Organo-nickel
(d) Ni 250 – 300°C

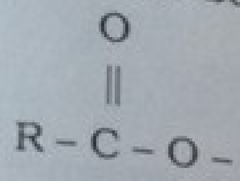
19. Mixture of catalysts $Cr_2O_3 + A\ell_2O_3 + SiO_2$ at 500°C are used when benzene is prepared from
(a) acetylene
(b) n-hexane
(c) Benzene sulphonic acid
(d) Sodium benzoate

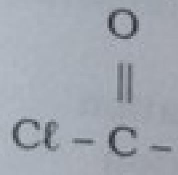
20. Which one of the following methods will not give benzene?
(a) Heating sod. Salt of Benzoic acid with soda lime
(b) Distilling phenol with Zn dust
(c) Chlorobenzene with NaOH at 360°C & 150atm.
(d) Hydrolysis of benzene sulphonic acid with super heated steam.

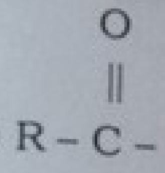
21. Which is fused cyclic aromatic compound
(a) diphenyl amine
(b) diphenyl methane
(c) naphthalene
(d) biphenyl

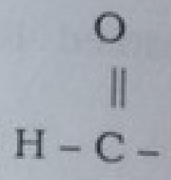
22. In Friedel Craft Alkylation, $A\ell C\ell_3$ is used to generate
(a) Strong nucleophile
(b) Weak nucleophile
(c) Strong electrophile
(d) Weak electrophile

23. Acylation of benzene is the introduction of ______ on benzene.

(a) 
$R-\overset{O}{\overset{\|}{C}}-O-$

(b) 
$C\ell-\overset{O}{\overset{\|}{C}}-$

(c) 
$R-\overset{O}{\overset{\|}{C}}-$

(d) 
$H-\overset{O}{\overset{\|}{C}}-$

24. Acetophenone is a
(a) Ether
(b) Ketone
(c) Aldehyde
(d) Ester

25. Reacting bromine with benzene in the presence of sunlight will result in
(a) The rupturing of benzene ring
(b) Substitution reaction
(c) Addition reaction
(d) No-reaction

26. Benzene does not undergo
(a) Substitution reaction
(b) Addition reaction
(c) Polymerization reactions
(d) Oxidation reactions

27. During sulphonation of benzene, H_2SO_4 generates the electrophile
(a) HSO_4^-
(b) SO_2
(c) SO_3
(d) H^+

28. Nitronium ion is
(a) NO_3
(b) NO
(c) NO_2^-
(d) NO_2^+

29. Which compound will readily undergo sulphonation?
(a) Benzene
(b) Nitro benzene
(c) Toluene
(d) Chlorobenzene

30. Benzene is heated in air with V_2O_5 at 450°C it undergoes
(a) Substitution reaction
(b) Addition reaction
(c) Elimination reaction
(d) Oxidation reaction

31. Which one of the following statement is not correct about benzene?
(a) On hydrogenation, 208 KJ/mole is liberated
(b) C-H bond length in benzene is $1.09\ A^{o}$
(c) Molecular mass of benzene is 78.108
(d) Resonance energy of benzene is 150.5 K Cal/mole

32. The preparation of benzene from acetylene can also be said as
(a) Oxidation
(b) Polymerization
(c) Dehydration
(d) Condensation

33. What is required other than anhydrous $A\ell C\ell_3$, when toluene is prepared Friedal craft reaction?
(a) C_6H_6
(b) $C_6H_6 + CH_3C\ell$
(c) $C_6H_5C_2H_5$
(d) $C_6H_5C\ell$ & CH_3Cl

34. Replacement of hydrogen of benzene by alkyl group in the presence of alk halide & aluminum chloride is known as
(a) Dow's process
(b) Friedel & Craft acylation
(c) Friedel & Craft alkylation
(d) Clemmenson reduction

35. Which one of the following radical is called benzyl radical?
(a) C_6H_5-
(b) C_6H_5-C
(c) C_6H_5-CH-
(d) $C_6H_5-CH_2-$

36. Which compound form benzoic acid on oxidation with acidified $KMnO_4$ o $K_2Cr_2O_7$
(a) Toluene
(b) Ethyl benzene
(c) n-propyl benzene
(d) All

37. Ozonolysis of benzene produces
(a) Glycol
(b) Glyoxal
(c) Vicinal diol
(d) Both b & c

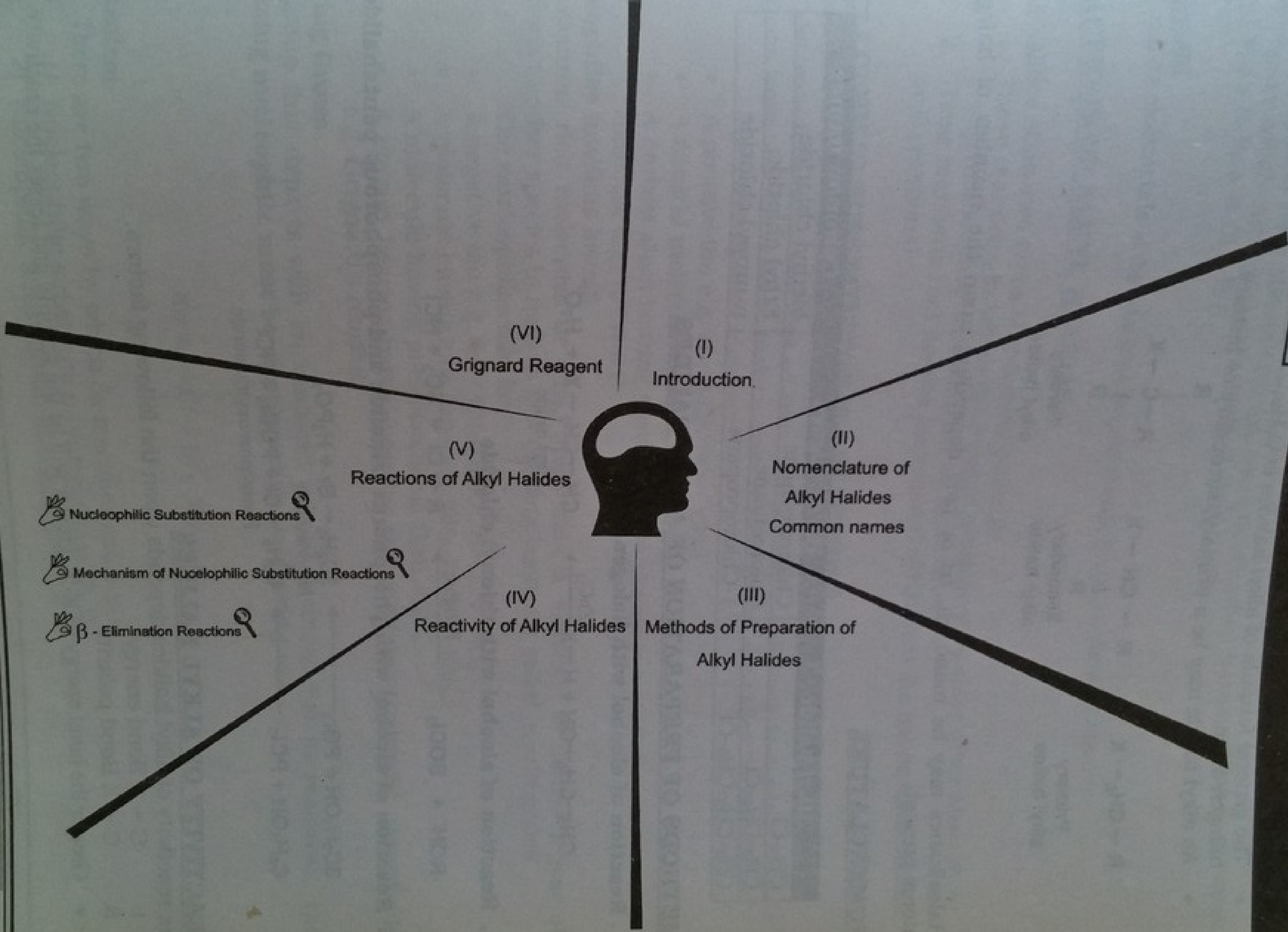
38. Which one of the following is benzal chloride?
(a) $C_6H_5\ CH_2C\ell$
(b) $C_6H_5\ CHC\ell_2$
(c) $C_6H_5-CH = CHC\ell$
(d) None of the above

39. What is the molecular formula of Benzenetriozonide?
(a) $C_6H_6O_9$
(b) $C_6H_5O_8$
(c) $C_6H_5O_9$
(d) $C_6H_6O_6$

40. The hydrolysis of Benzenetrizonide will yield three moles of
(a) Glyoxime
(b) Benzaldehyde
(c) Glycol
(d) Glyoxal

Chapter 10

ALKYL HALIDES


(VI)
Grignard Reagent
(I)
Introduction.
(V)
Reactions of Alkyl Halides
(II)
Nomenclature of
Alkyl Halides
Common names
Nucleophilic Substitution Reactions
Mechanism of Nucelophilic Substitution Reactions
β - Elimination Reactions
(IV)
Reactivity of Alkyl Halides
(III)
Methods of Preparation of
Alkyl Halides

Chapter 10

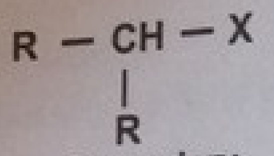
INTRODUCTION

Those organic compounds which are derived from the hydrocarbons by the replacement of one hydrogen atom by the halogen atoms are called alkyl halides.

- The general formula of alkyl halides is $C_nH_{2n+1}X$ or R-X in which 'X' stands for a halogen atom.
- An alkyl halide may be a primary, secondary or tertiary.

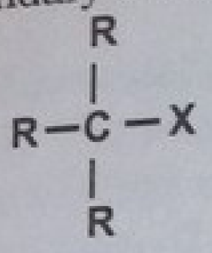
$R-CH_2-X$

Primary
alkyl halide



$$R-\underset{\displaystyle R}{\underset{|}{CH}}-X$$

Secondary
alkyl halide



$$R-\underset{\displaystyle R}{\underset{|}{\overset{\displaystyle R}{\overset{|}{C}}}}-X$$

Tertiary
alkyl halide

Haloalkanes may be mono, di, tri or poly depending upon the number of halogen atoms present.

NOMENCLATURE

Alkyl halide	IUPAC names	Common names
CH_3-Cl	Chloromethane	Methyl chloride
CH_3-CH_2-Cl	Chloroethane	Ethyl chloride
CH_3-CH_2-CH_2-Cl	1-Chloropropane	n-propyl chloride

METHODS OF PREPARATION OF ALKYL HALIDES

1. Reaction of alcohol with halogen acids

$$CH_3-CH_2-OH + H-X \xrightarrow{ZnCl_2} \underset{\text{Ethyl halide}}{CH_3-CH_2-X} + H_2O$$

2. Reaction of alcohol with thionyl chloride

$$ROH + SOCl_2 \xrightarrow{\text{Pyridine}} R-Cl + SO_2 + HCl$$

3. Reaction of alcohol with phosphorus trihalide and phosphorous pentahalide

$$3C_2H_5OH + PBr_3 \longrightarrow \underset{\text{Ethyl bromide}}{3C_2H_5-Br} + H_3PO_3$$

$$C_2H_5OH + PCl_5 \longrightarrow C_2H_5-Cl + \underset{\text{Phosphorus oxytrichloride}}{POCl_3} + HCl$$

REACTIVITY OF ALKYL HALIDES

The reactivity of alkyl halides depends upon the following factors,

i. C – X Bond energy
ii. C – X Bond polarity

- Greater the bond energy of R-X, greater will be the stability and lesser the reactivity.

- Greater EN difference (bond polarity) of R-X, greater will be the stability and lesser the reactivity.

Conclusion

Experiments have shown that the strength of carbon halogen bond is the main factor which decides the reactivity of alkyl halides.

R-I > R-Br > R-Cl > R-F

Important

If an electrophile is the attacking reagent then R-F with be the most reactive.

REACTIONS OF ALKYL HALIDES

Alkyl halides show two types of reactions generally.

1. Those reactions in which the halogen is replaced by some other atom or a group (nucleophilic substitution, or S_N reactions)
2. Those reactions that involve the removal of HX from the halide (elimination, or E reactions)

NUCLEOPHILIC SUBSTITUTION (S_N) REACTIONS

Electrophiles (electron loving).

The electron-deficient molecules or ions, which have a tendency to accept a pair of electrons from other species to make a new covalent bond, are called "electrophiles"

The electrophiles may be:

- A positive ion e.g. H^+, H_3O^+, NO_2^+, CH_3^+
- A neutral molecule e.g. SO_3, $AlCl_3$, BF_3.
- A carbon atom bearing partial positive charge in a partially ionic covalent molecule e.g. R-CH = O$^-$.

Nuceophiles (nucleus loving)

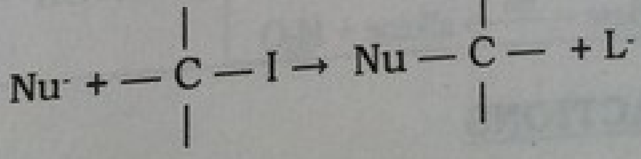
The electron rich molecules or ions, which have a tendency to donate a pair of electrons to other species to make a new covalent bond, are called "nucleophiles".

The nucleophiles may be:

- A negative ion e.g. OH^-, CH_3COO^-, Br^-, CN^-, NO_3^{-1}
- A molecule having lone pairs e.g. NH_3, H_2O, $R{-}NH_2$.
- A molecule having pi-electrons e.g. C_2H_2, C_2H_4.
- A carbon bearing partial negative charge in organometallic compounds e.g. Grignard's reagent.

Leaving Group

The group that departs with an unshared pair of electrons. **For S_N reactions, the incoming nucleophile must be stronger than the leaving one.**



$$Nu^- + -\overset{|}{\underset{|}{C}}-I \rightarrow Nu-\overset{|}{\underset{|}{C}}- + L^-$$

Mechanism

There are two ways by which S_N reactions can occur:

1) Nucleophilic substitution unimolecular (S_N1)
2) Nucleophilic substitution bimolecular (S_N2)

	S_N1 REACTIONS	S_N2 REACTIONS
1	Molecularity of SN_1 reaction is one.	Molecularity of SN_2 reaction is two.
2	The reaction is: $R—X \rightarrow R^+ + X^-$ (slow) $R^+ + Nu^- \rightarrow R—Nu$ (fast)	The reaction is : $R—X + Nu^- \rightarrow R—Nu + X^-$ (Slow)
3	Rate α $[R—X]$ Rate = $k[R—X]$	Rate α $[R—X][Nu^-]$ Rate = $k[R—X][Nu^-]$
4	Coming nucleophile may attack from any side.	Coming nucleophile only attacks from backside.
5	Tertiary alkyl halides generally give S_N1 reactions.	Primary alkyl halides generally give S_N2 reactions.
6	The product is a racemic mixture i.e. 50% inversion of configuration	The product with 100% inversion of configuration.
7	Order of reaction is one.	Order of reaction is two.
8	It is a two steps mechanism.	It is a single step mechanism.
9	It is favoured in polar solvents.	It is favoured in non polar solvent.

Note:-

Secondary alkyl halide can give both reactions depending upon the structure of alkyl group or nature of the solvent.

β-ELIMINATION OR E-REACTION

The reactions where the attack takes place on an electrophilic hydrogen attached to β-carbon of alkyl halide, resulting in formation of alkene are known as β-reactions.

- E and S_N reactions can take place simultaneously and often competition occurs.
- E can take place in two ways:

	E1 REACTIONS	E2 REACTIONS
1	Two steps mechanism	One step mechanism
2	Molecularity is one.	Molecularity is two.
3	Rate α $[R—X]$ Rate = $k[R—X]$	Rate α $[R—X][Base]$ Rate = $k[R—X][Base]$
4	Tertiary alkyl halides generally give E_1 reactions.	Primary alkyl halides generally give E_2 reactions.
5	Order of reaction is one.	Order of reaction is two.
6	The reaction is: $R—X \xrightarrow{slow} carbocation + X^-$ $carbocation + Base \xrightarrow{fast} alkene + H_2O$	The reaction is: $R—X + OH^- \xrightarrow{slow} Alkene + H_2O + X^-$

EXAMPLES OF S_N REACTIONS

$$C_2H_5—Br + OH^- \longrightarrow Br^- + C_2H_5—OH$$

$$2\,C_2H_5—Br + 2Na \xrightarrow{ether} \underbrace{C_2H_5—C_2H_5}_{\text{n-butane}} + 2NaBr$$

$$C_2H_5-Br + [2H] \xrightarrow{Zn/dil.HCl} C_2H_6 + HBr$$

$$C_2H_5-Br + CN^- \longrightarrow C_2H_5-CN + Br^-$$

Ethyl nitrile

$$4CH_3-Cl + Na_4\,Pb \longrightarrow (CH_3)_4\,Pb + 4NaCl$$

Sodium lead alloy — Tetra methyl lead

$$4C_2H_5-Cl + Na_4\,Pb \longrightarrow (C_2H_5)_4\,Pb + 4NaCl$$

Sodium lead alloy — Tetra ethyl lead

$$C_2H_5\ Br + NH_3 \longrightarrow C_2H_5-NH_2 + HBr$$

Ethyl amine

$$C_2H_5-Br + C_2H_5-NH_2 \longrightarrow (C_2H_5)_2\,NH + HBr$$

diethyl amine

$$(C_2H_5)_2\,NH + C_2H_5Br \longrightarrow (C_2H_5)_3N + HBr$$

Triethyl amine

$$(C_2H_5)_3N + C_2H_5Br \longrightarrow (C_2H_5)_4N^+ + HBr$$

Quaternary ethyl ammonium bromide

$$C_2H_5Br + I^- \longrightarrow C_2H_5\,I + Br^-$$

Ethyl iodide

$$C_2H_5Br + NO_2^- \longrightarrow C_2H_5NO_2 + Br^-$$

nitroethane

$$C_2H_5\,Br + CH_3O^- \longrightarrow C_2H_5-O-CH_3 + Br^-$$

Ethyl methyl ether

$$C_2H_5-Br + SH^- \longrightarrow C_2H_5-SH + Br^-$$

Ethyl thioalcohol

$$C_2H_5-Br + CH_3COONa \longrightarrow CH_3COOC_2H_5 + NaBr$$

Ethyl acetate

PRACTICE EXERCISE

20 mins Time Yourself

1. What will be the products when reactants are alcohol & thionyl chloride in the presence of pyridine?
(a) $RC\ell+S+HC\ell$
(b) $RC\ell+SO_2+HC\ell$
(c) $RC\ell+SO_2+H_2O$
(d) $RC\ell+S+H_2O$

2. Which C-X bond has the highest bond energy per mole?
(a) C–F
(b) C–Cℓ
(c) C–Br
(d) C–I

3. Which alkyl halide has the highest reactivity, for a particular alkyl group?
(a) R–F
(b) R–Cℓ
(c) R–Br
(d) R–I

4. Ethyl chloride with nascent hydrogen produces
(a) methane
(b) ethane
(c) propane
(d) butane

5. Which one is not a nucleophile?
(a) $C_2H_5O^-$
(b) SCN^-
(c) NH_3
(d) H_3C^+

6. The number of molecules taking part in the rate determining step is called
(a) Order of reaction
(b) Rate of reaction
(c) Mole of a reaction
(d) Extent of a reaction

7. During S_N2 mechanism, carbon atom changes its state of hybridization as
(a) $sp \to sp^2$
(b) $sp^2 \to sp^3$
(c) $sp^3 \to sp$
(d) $sp^3 \to sp^2$

8. What will be the order of reaction of a reaction whose rate can be expressed as R = K [A] [B]?
(a) Zero
(b) One
(c) Two
(d) Three

9. Which one among the following is not a good leaving group?
(a) HSO_4^-
(b) $C\ell^-$
(c) OH^-
(d) Br^-

10. What is the order of kinetics in the S_N1 mechanism?
(a) Zero
(b) First
(c) Second
(d) Third

11. Which alkyl halide out of the following may follow both S_N1 and S_N2 mechanism?
(a) $CH_3–X$
(b) $(CH_3)_3\,C – CH_2 – X$
(c) $(CH_3)_2\,CH – X$
(d) $(CH_3)_3\,C – X$

12. In elimination reactions of alkyl halide, which site is more susceptible for the attack of base
(a) α-carbon
(b) β-carbon
(c) α-hydrogen
(d) β-hydrogen

13. When two moles of ethyl chloride react with two moles of sodium in the presence of ether, what will be formed?
(a) 2 moles of ethane (b) 1 mole of ethane
(c) 2 moles of butane (d) 1 mole of butane

14. The ether used in Wurtz synthesis is
(a) acidic (b) basic
(c) aqueous (d) dry

15. When CO_2 is made to react with ethyl magnesium iodide, followed by acid hydrolysis, the product formed is
(a) propane (b) propanoic acid
(c) propanal (d) propanol

16. Grignard reagent is reactive due to
(a) the presence of halogen atom (b) the presence of magnesium atom
(c) the polarity of C-Mg bond (d) all

17. S_N2 reaction can be best carried out with
(a) primary alkyl halide (b) secondary alkyl halide
(c) tertiary alkyl halide (d) all

18. Elimination bimolecular reactions involve
(a) first order kinetics (b) second order kinetics
(c) third order kinetics (d) zero order kinetics

19. For which mechanisms, the first step involved is the same?
(a) E1+E2 (b) E2 and S_N2
(c) E1 and S_N1 (d) S_N1 and S_N2

20. The rate of E1 reaction depends upon
(a) the concentration of substrate
(b) the concentration of nucleophile
(c) the concentration of substrate as well as nucleophile
(d) base the concentration of substrate as well as nucleophile

21. Alkyl halides are considered to be very reactive compounds towards nucleophile because
(a) they have an electrophilic carbon
(b) they have an electrophilic carbon & a good leaving group
(c) they have an electrophilic carbon & a bad leaving group
(d) they have a nucleophilic carbon & a good leaving group

22. Which one of the following species is not an electrophile?
(a) NH_3 (b) Br^+
(c) H^+ (d) BF_3

23. Which one of the following reactants will be required to form straight chain alcohol by using Grignard reagent
(a) formaldehyde (b) ketone
(c) ethylene epoxide (d) both a & c

24. Which one of the following alcohols will be formed when ethyl magnesium bromide reacts with acetone?
(a) primary alcohol (b) secondary alcohol
(c) tertiary alcohol (d) dihydric alcohol

25. Which one of the following molecules does not form alcohol when reacts with Grignard reagent?
(a) formaldehyde (b) acetaldehyde
(c) propanone (d) carbondioxide

26. In primary alkyl halides, the halogen atom is attached to a carbon, which is further attached to how many carbon atoms

(a) two
(b) three
(c) one
(d) four

27. Ethylene epoxide treated with Grignard's reagent followed by acid hydrolysis yield

(a) primary alcohol
(b) secondary alcohol
(c) tertiary alcohol
(d) dihydric alcohol

8. The best method of preparation of alkyl halides, is a reaction of alcohol with

(a) Zn / HCl
(b) $SOCl_2$ / Pyridine
(c) PCl_3
(d) PCl_5

9. Alkyl halides undergo a type of reaction

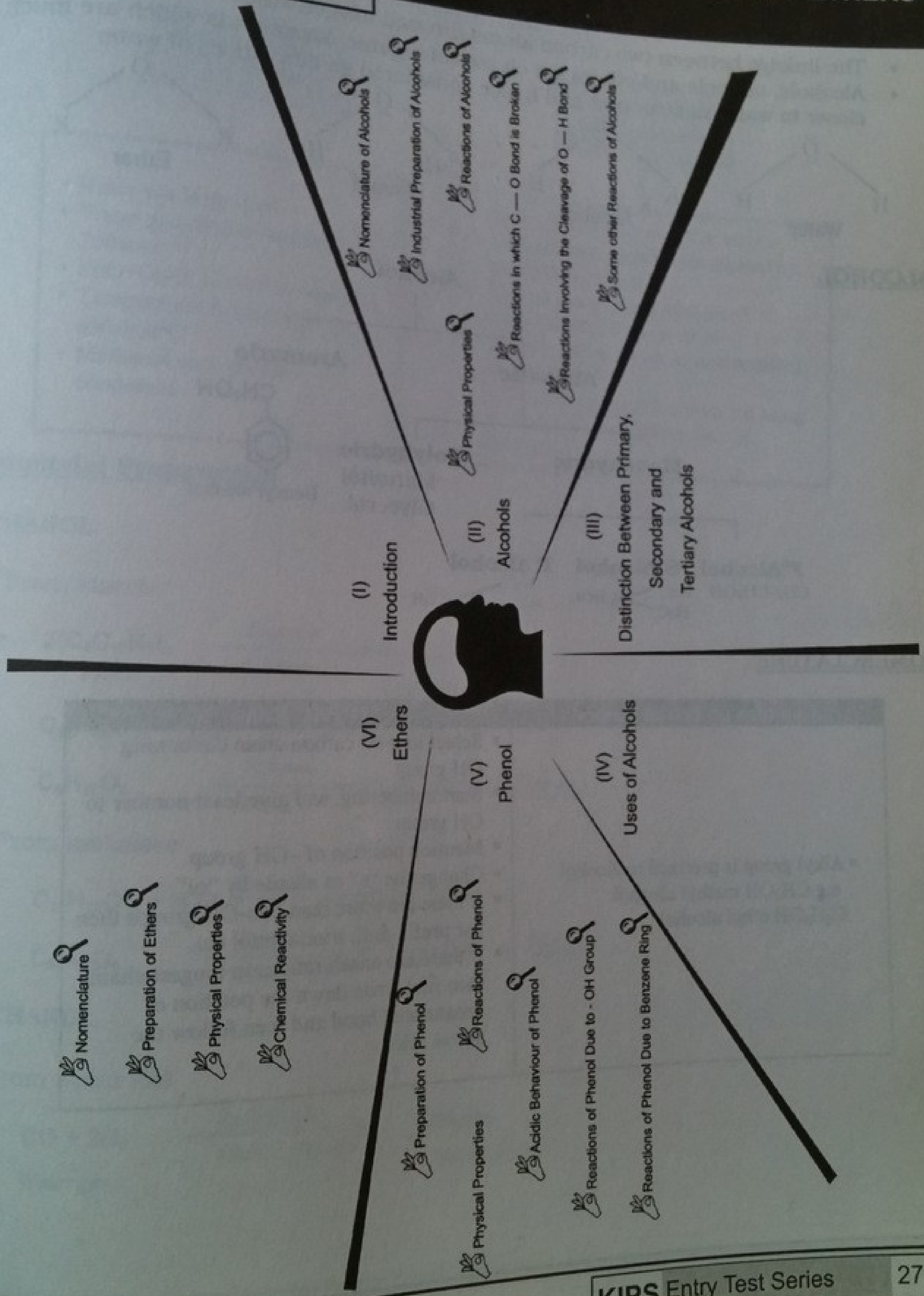
(a) Nucleophilic substitution
(b) Nucleophilic addition
(c) Elimination
(d) both a & c

50% inversion of configuration of molecules take place in a

(a) E_1 – reaction
(b) E_2 – reaction
(c) S_N1 – reaction
(d) S_N2 – reaction

Chapter 11

ALCOHOLS, PHENOLS AND ETHERS



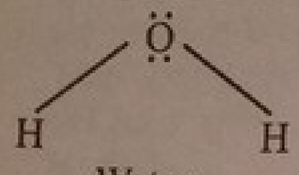
(I) Introduction
(II) Alcohols
Nomenclature of Alcohols
Industrial Preparation of Alcohols
Reactions of Alcohols
Physical Properties
Reactions in which C — O Bond is Broken
Reactions Involving the Cleavage of O — H Bond
Some other Reactions of Alcohols
(III) Distinction Between Primary, Secondary and Tertiary Alcohols
(IV) Uses of Alcohols
(V) Phenol
Preparation of Phenol
Physical Properties
Reactions of Phenol
Acidic Behaviour of Phenol
Reactions of Phenol Due to - OH Group
Reactions of Phenol Due to Benzene Ring
(VI) Ethers
Nomenclature
Preparation of Ethers
Physical Properties
Chemical Reactivity

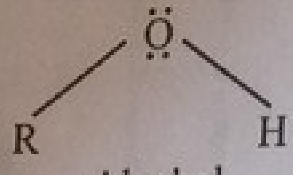
Chapter 11

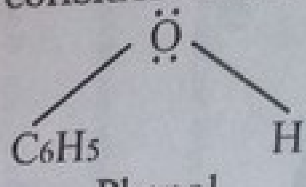
Alcohols, Phenols & Ethers

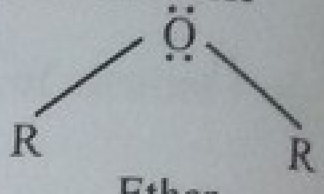
INTRODUCTION

- When H of alkane is replaced by –OH group, then it is called alcohol.
- When the H of benzene ring is replaced by –OH group, then it is called phenol.
- The linkage between two carbon atoms through oxygen atom is called ether.
- Alcohols, phenols and ethers are classes of organic compounds which are much closer to water in structure and hence considered as derivatives of water

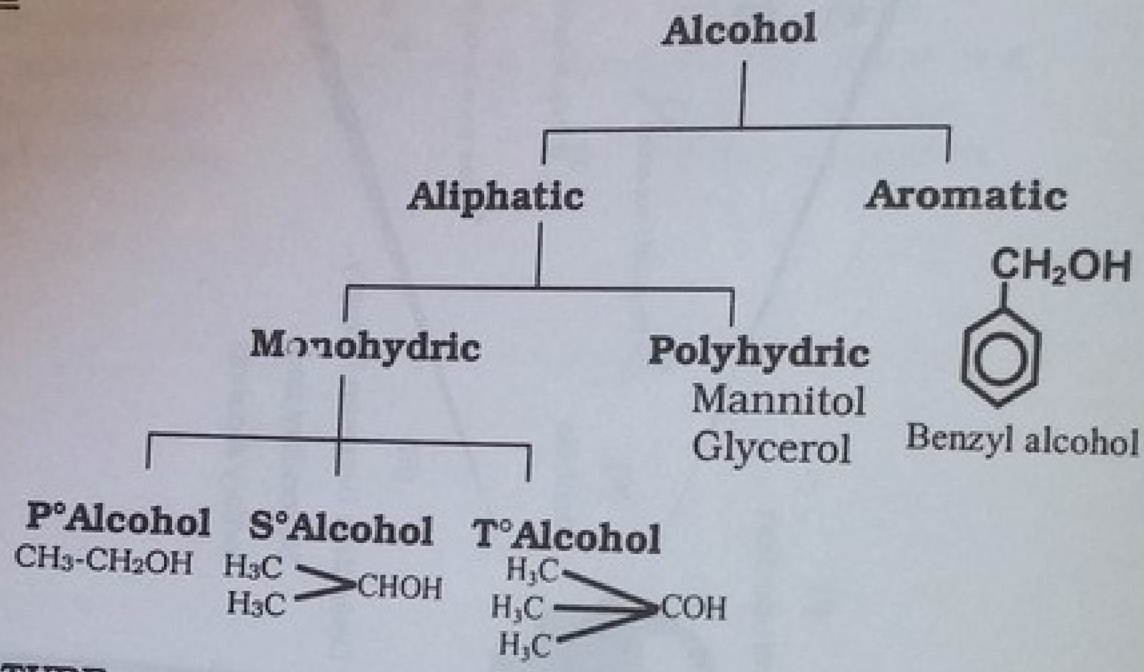

Water


Alcohol


Phenol


Ether

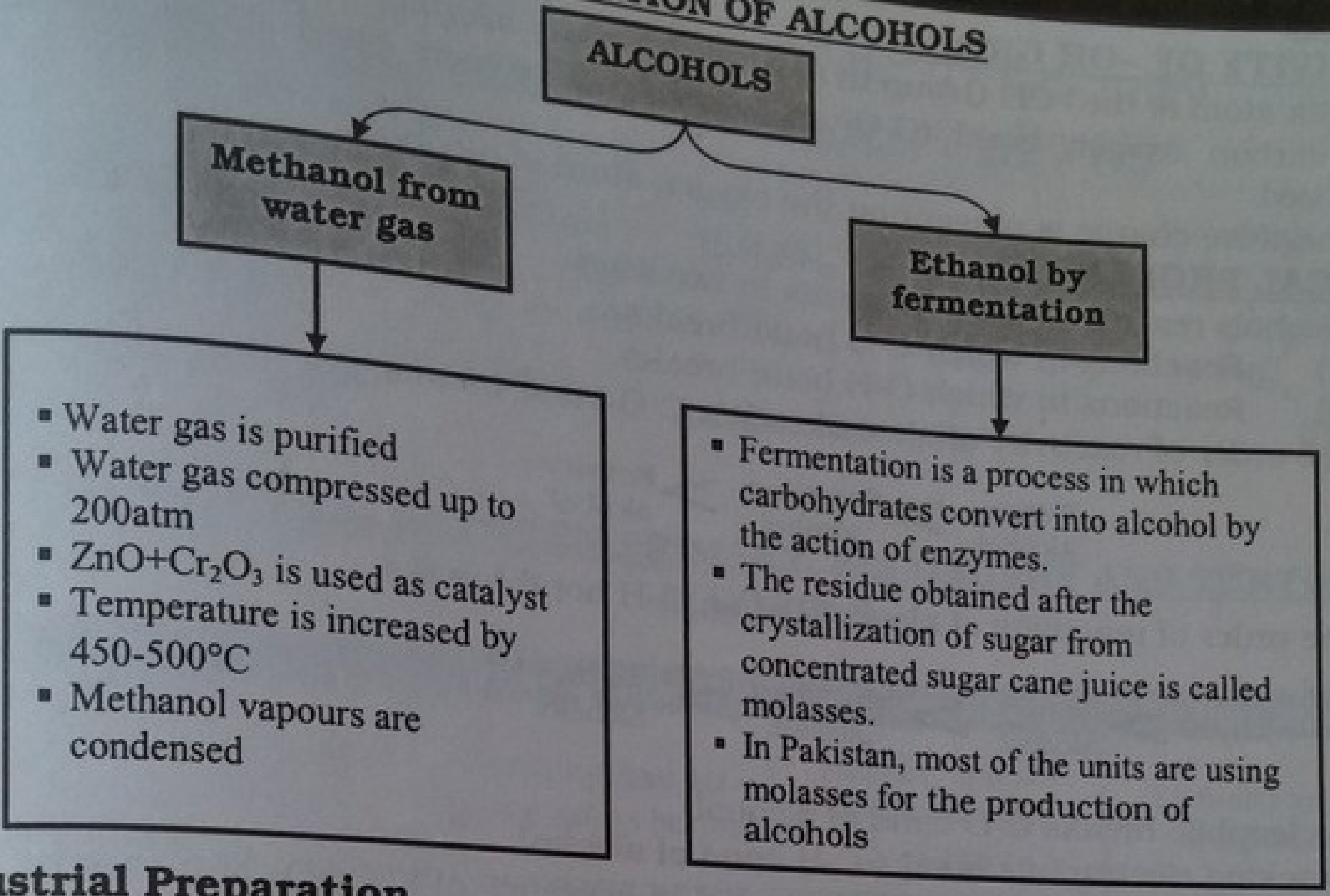
ALCOHOL



NOMENCLATURE

Common or Trivial Names	IUPAC Rules
▪ Alkyl group is prefixed to alcohol e.g CH_3OH methyl alcohol C_2H_5OH ethyl alcohol	▪ Select longest carbon chain containing –OH group ▪ Start numbering, and give least number to OH group ▪ Mention position of –OH group ▪ Change the "e" of alkane by "ol" ▪ If there are more than two-OH groups then use prefix diol, triol, tetraol etc. ▪ If there are unsaturations in longest chain then first write down the position of unsaturated bond and then follow the above rules.

PREPARATION OF ALCOHOLS



ALCOHOLS

Methanol from water gas

- Water gas is purified
- Water gas compressed up to 200atm
- ZnO+Cr_2O_3 is used as catalyst
- Temperature is increased by 450-500°C
- Methanol vapours are condensed

Ethanol by fermentation

- Fermentation is a process in which carbohydrates convert into alcohol by the action of enzymes.
- The residue obtained after the crystallization of sugar from concentrated sugar cane juice is called molasses.
- In Pakistan, most of the units are using molasses for the production of alcohols

Industrial Preparation

ETHANOL

- From starch

$$\underset{\text{Starch}}{2(C_6C_{10}H_5)_n} \xrightarrow[\text{Yeast}]{\text{Diastase}} \underset{\text{Malt sugar}}{nC_{12}H_{22}O_{11}}$$

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{Yeast}]{\text{Maltose}} 2C_6H_{12}O_6$$

$$C_6H_{12}O_6 \xrightarrow[\text{Yeast}]{\text{Zymase}} 2C_2H_5-OH + 2CO_2$$

- From molasses

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{Yeast}]{\text{Invertase}} 2C_6H_{12}O_6$$

$$C_6H_{12}O_6 \xrightarrow[\text{Yeast}]{\text{Zymase}} 2C_2H_5-OH + 2CO_2$$

METHANOL

- From water gas

$$\underset{\text{Water gas}}{CO + 2H_2} \xrightarrow[\text{450°C ; 200atm}]{ZnO/Cr_2O_3} \underset{\text{Methyl alcohol}}{CH_3OH}$$

REACTIVITY OF –OH GROUP

- Oxygen atom of the –OH Group in alcohols is sp^3 hybridized
- The carbon oxygen bond (C-O) and hydrogen oxygen bond (O-H) are highly polarized.
- The negative charge is present on the oxygen atom of alcohol.

CHEMICAL PROPERTIES

- Alcohols react with other reagents in two ways
  (1) Reactions in which C-O bond breaks.
  (2) Reactions in which O-H bond breaks.
- The order of reactivity of alcohols when C-O bond breaks

Tertiary alcohol > Secondary alcohol > Primary alcohol

- The order of reactivity of alcohols when O-H bond breaks

CH_3OH > Primary alcohol > Secondary alcohol > Tertiary alcholol

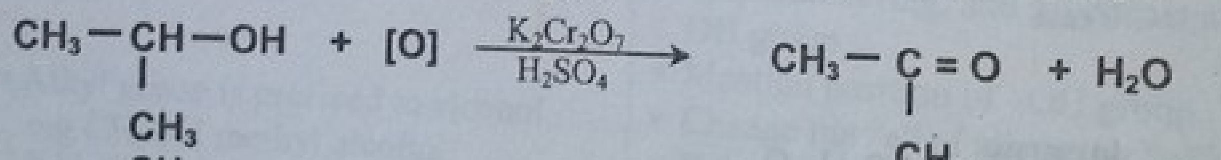
- Nucleophile breaks C-O bond of alcohol.
- Attacking electrophile breaks C-H bond of alcohol.
- Catalytic oxidation of secondary alcohol in presence of $K_2Cr_2O_7$ and H_2SO_4, converts it into ketones; while same reaction of tertiary alcohol gives alkenes.
- On heating with H_2SO_4 (conc.), alcohol changes to alkene.

REACTIONS OF ALCOHOLS

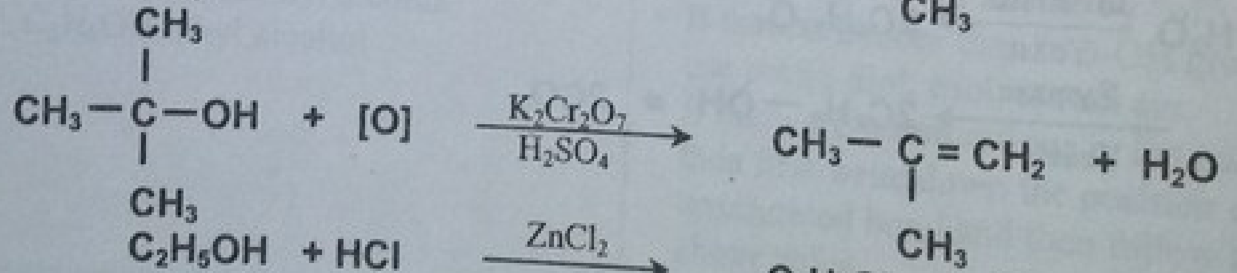
$$3C_2H_5OH + PCl_3 \longrightarrow 3C_2H_5Cl + \underset{\text{Phosphorous acid}}{H_3PO_3}$$

$$C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + HCl + \underset{\text{Phosphorous oxytrichloride}}{POCl_3}$$

$$C_2H_5OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-CHO + H_2O$$



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=O + H_2O$$



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2 + H_2O$$

$$C_2H_5OH + HCl \xrightarrow{ZnCl_2} C_2H_5Cl + H_2O$$

$$C_2H_5OH + CH_3COOH \xrightarrow{H_2SO_4} CH_3COOC_2H_5 + H_2O$$

$$C_2H_5OH \xrightarrow[180°C]{Conc.\ H_2SO_4} CH_2=CH_2 + H_2O$$

$$2C_2H_5OH \xrightarrow[\text{Conc. } H_2SO_4]{140^\circ C} C_2H_5-O-C_2H_5 + H_2O$$

$$\underset{\text{Thionyl chloride}}{C_2H_5OH + SOCl_2} \xrightarrow{\text{Pyridine}} C_2H_5Cl + SO_2 + HCl$$

$$C_2H_5OH + NH_3 \xrightarrow{ThO_2} C_2H_5NH_2 + H_2O$$

$$C_2H_5-Mg-I + C_2H_5-OH \xrightarrow{\text{ether}} CH_3-CH_3 + Mg\genfrac{}{}{0pt}{}{I}{OC_2H_5}$$

$$C_2H_5OH + 2Na \xrightarrow{\text{Ethanol}} C_2H_5ONa + H_2$$

DISTINCTION BETWEEN PRIMARY, SECONDARY AND TERTIARY ALCOHOLS

Tests	Primary alcohol	Secondary alcohols	Tertiary alcohols
Lucas Test: To the alcohol add concentrated HCl and $ZnCl_2$	Turbidity does not appear but on heating	Turbidity appears after some times 5 – 10 min	Turbidity appears immediately
Dichromate Test (Oxidation) To the alcohol add a mixture of $K_2Cr_2O_7$ and concentrated H_2SO_4	The orange solution of $K_2Cr_2O_7$ becomes green and aldehydes are produced	The orange solution of $K_2Cr_2O_7$ becomes green and ketones are produced	Solution remains orange as on dehydration alkene is formed

DISTINCTION BETWEEN METHANOL AND ETHANOL

Ethanol gives iodoform with iodine in the presence of NaOH. Formation of yellow crystals of iodoform (CHI_3) indicate that the alcohol is ethanol

$$C_2H_5OH + 4I_2 + 6NaOH \longrightarrow CHI_3 + HCOONa + 5NaI + 5H_2O$$

Methanol does not give iodoform test due to lack of alpha hydrogen

$$CH_3OH + I_2 + NaOH \longrightarrow \text{No yellow ppt}$$

USES OF ALCOHOLS

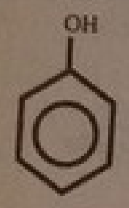
Methanol	Ethanol
• It is used as a solvent for fats, oils, paints and varnishes • It is used as antifreeze in the radiators of automobiles • It is used for denaturing of alcohol	• It is used as a ➢ Solvent ➢ Drinking ➢ Fuel • It is used in pharmaceutical preparations • It is used as a preservative for biological specimen

PHENOL

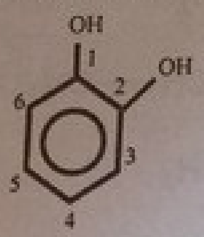
Aromatic compounds which contain one or more –OH groups directly attached with carbon of benzene ring are called Phenols.

Simplest Phenol

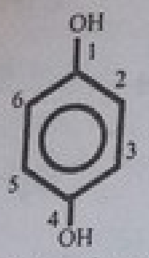
Carbolic acid (Benzenol) (C_6H_5OH). It was first obtained from coaltar by **Runge in 1834.**



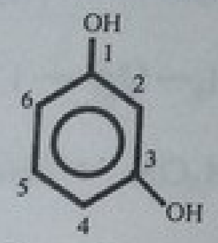
Phenol



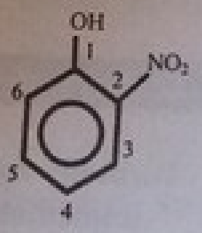
1,2-Dihydroxy benzene
o-Hydroxyl phenol
(catechol)



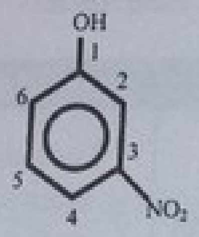
1,4-Dihydroxy benzene
p-hydroxy phenol
(hydroquinone)



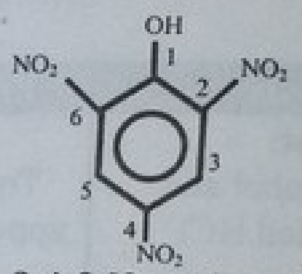
1,3-Dihydroxy benzene
m-dihydroxy phenol
(resorcinol)



2-Nitrophenol
O-Nitrophenol



m-Nitrophenol

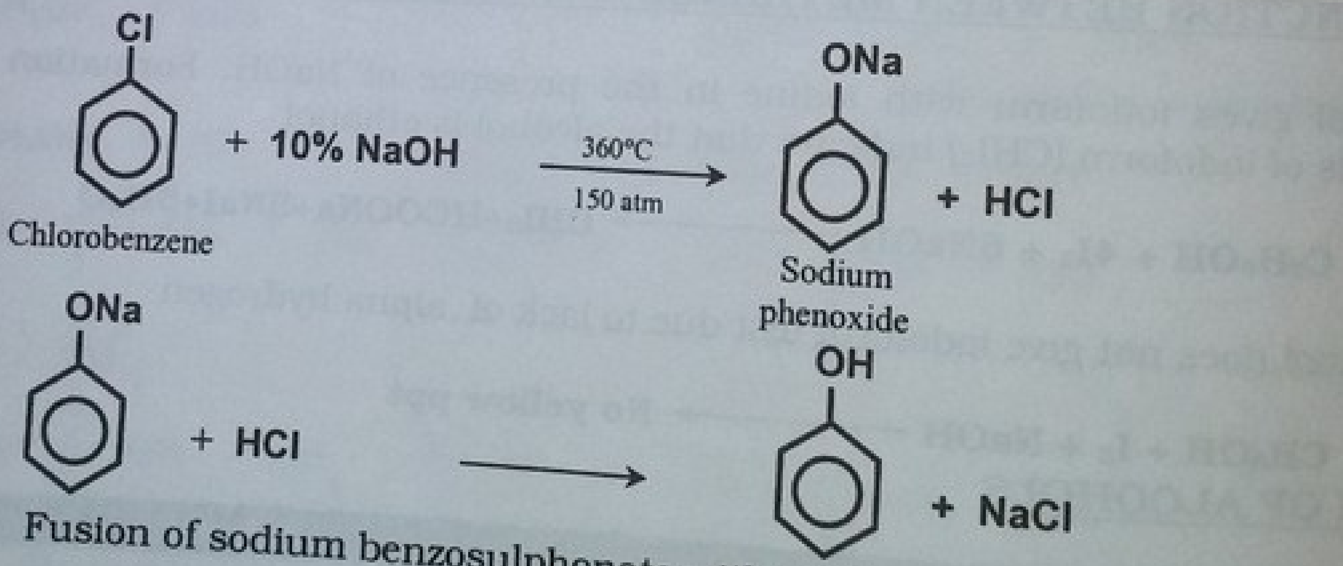


2,4,6-Nitrophenol
(picric acid)

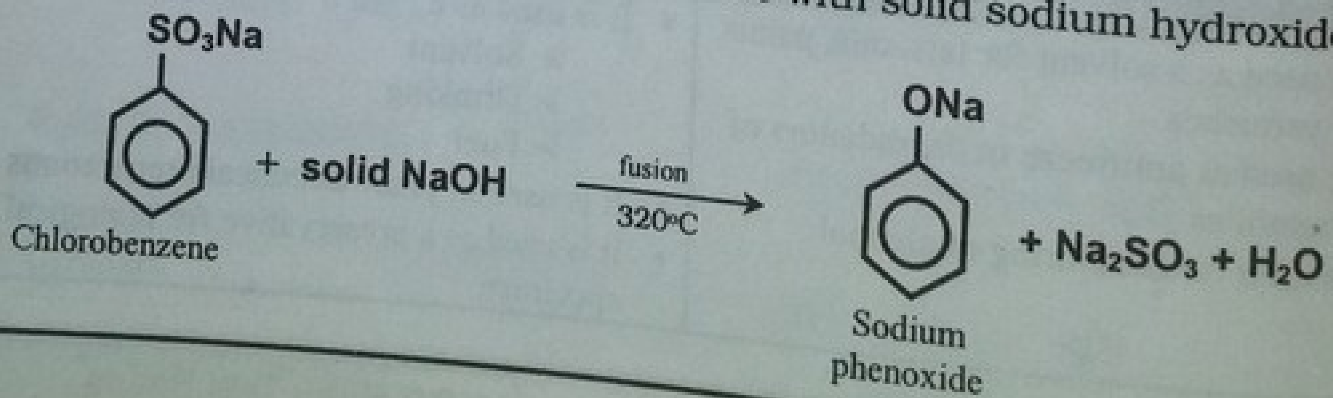
PREPARATION OF PHENOL

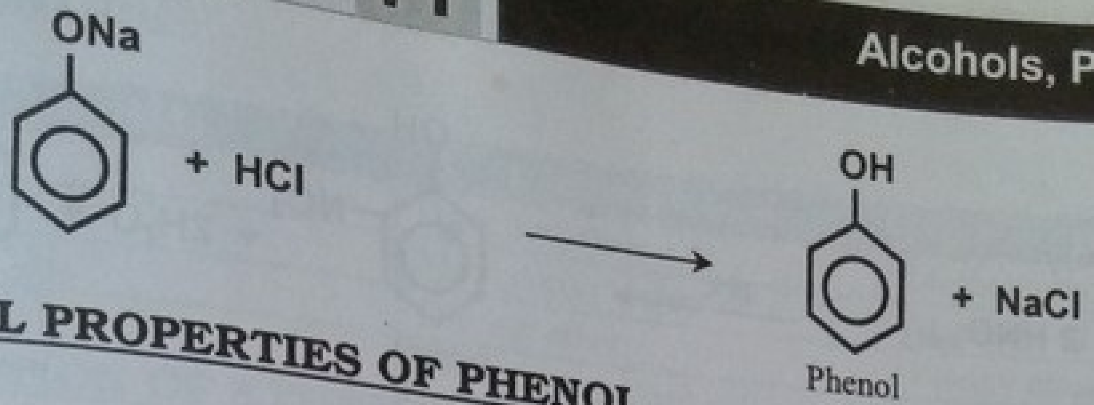
Source of reactant	Remarks
From chloro benzene(Dow's method)	▪ 10% NaOH is used ▪ Reaction completes in two steps
From sodium salt of sulphonic acid	Phenol is recovered by distillation

Dow's Process



Fusion of sodium benzosulphonate with solid sodium hydroxide





Phenol

PHYSICAL PROPERTIES OF PHENOL

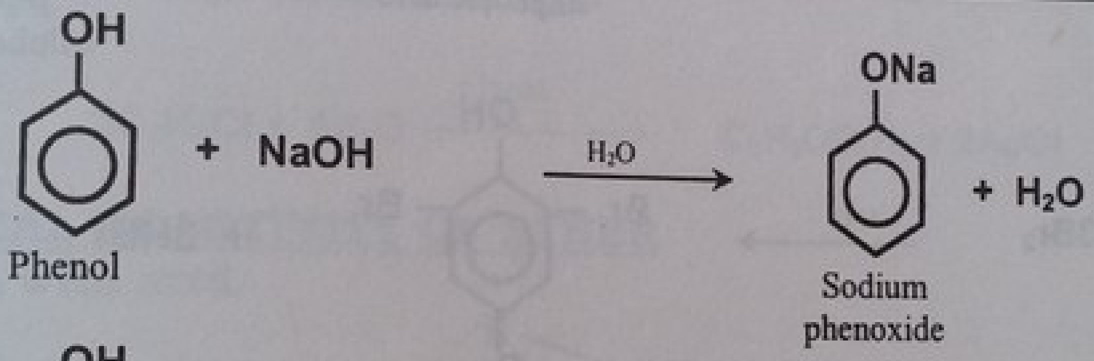
- It is a colourless, crystalline, deliquescent solid with characteristic phenolic odour.
- Its melting point is 41°C and boiling point is 182°C.
- It is sparingly soluble in water at room temperature but completely soluble above 68.5°C.

REACTIONS OF PHENOL

Phenol shows two types of reactions

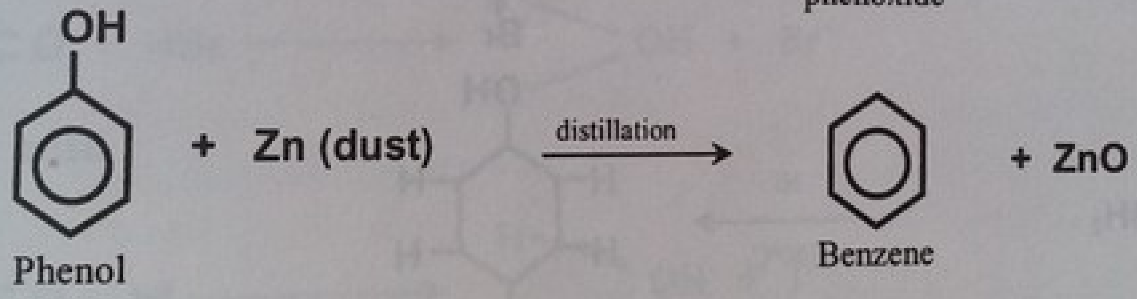
(i) REACTION OF PHENOL DUE TO –OH GROUP

Nature of reaction	Remarks
Salt formation	Phenoxides are formed
Ester formation	Reaction takes place in basic media
Reduction with Zn	Benzene is obtained



Phenol

Sodium phenoxide

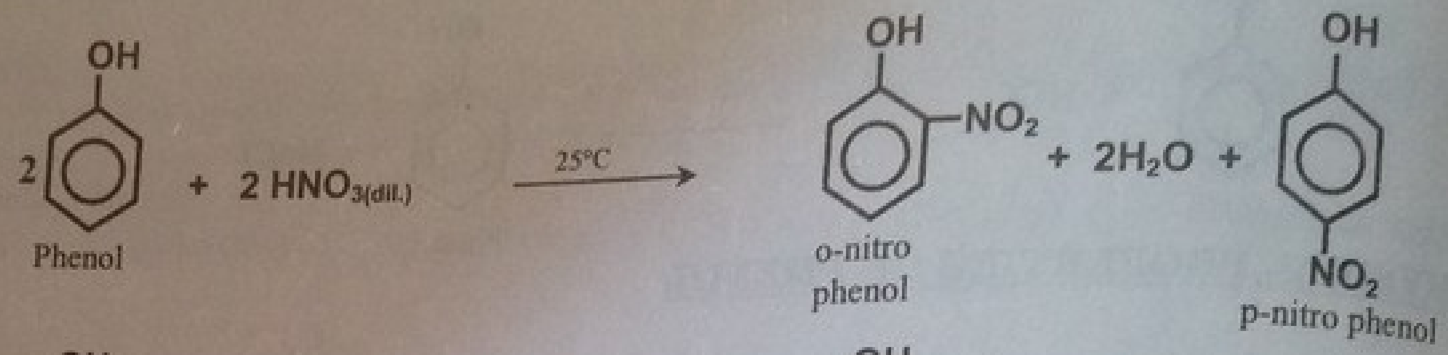


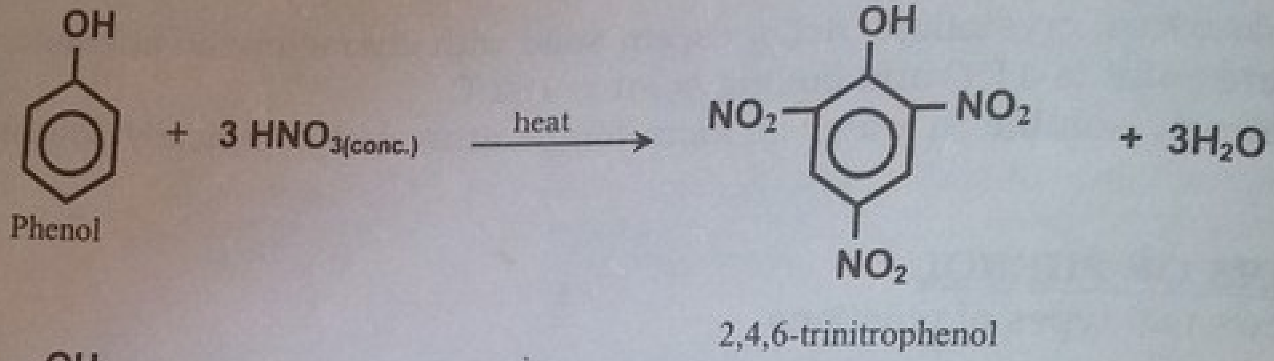
Phenol

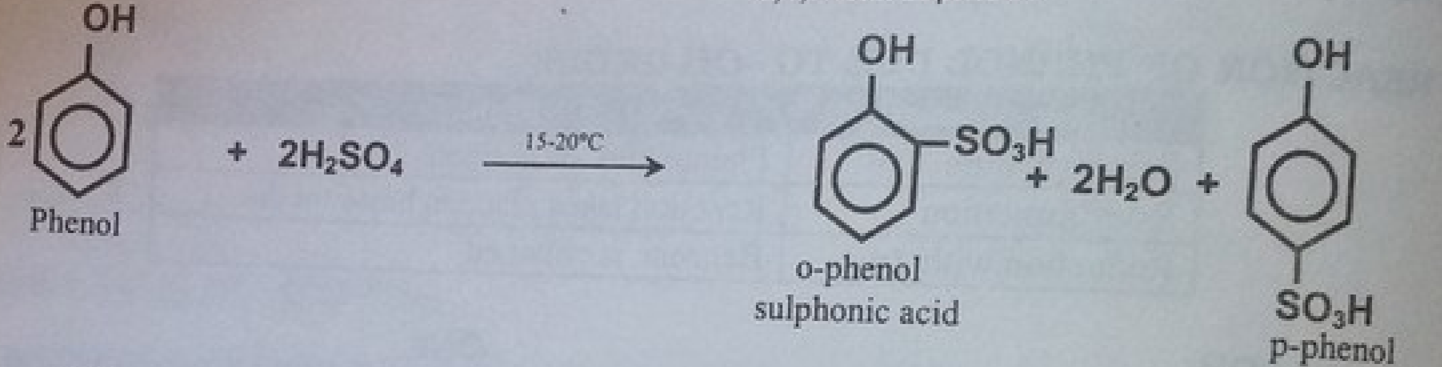
Benzene

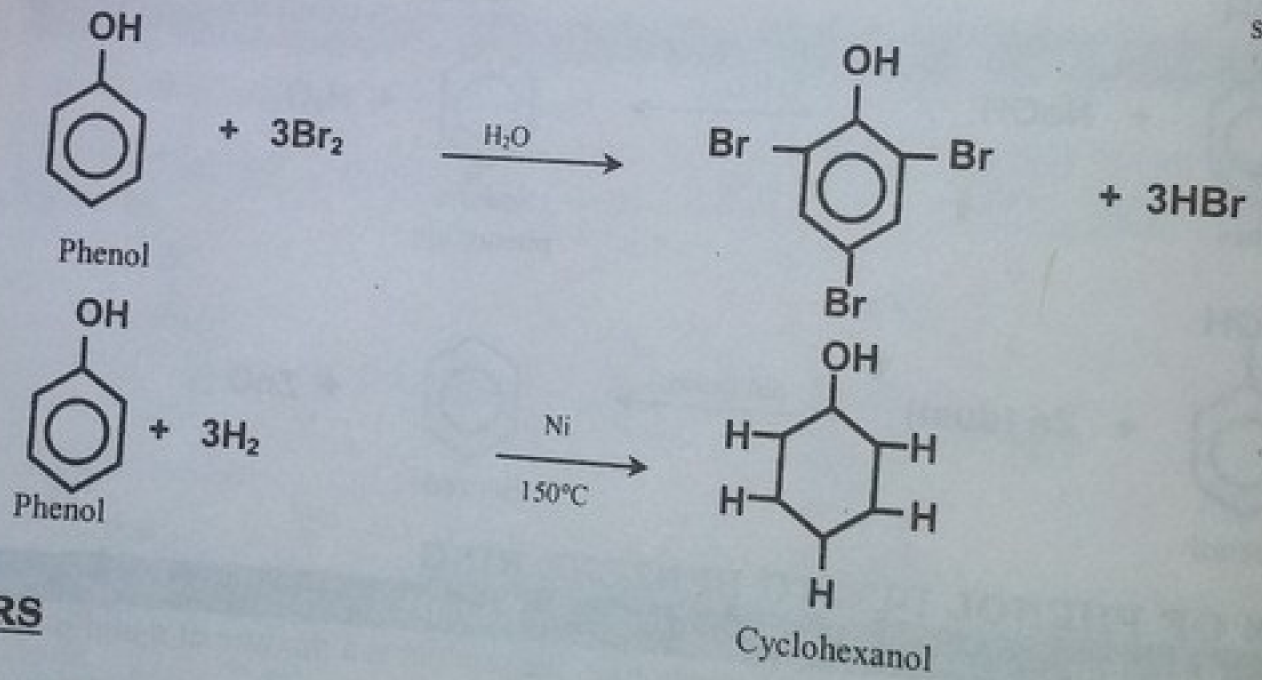
REACTION OF PHENOL DUE TO BENZENE RING

Reaction	Remarks
Nitration	▪ At room temperature, the product is a mixture of o-and p-nitrophenol with dil. HNO_3 ▪ At higher temperature, the product is picric acid with concentrated HNO_3
Sulphonation	Introduction of HSO_3^- is called sulphonation a mixture of ortho and para products at 15 to 20°C
Halogenation	White ppt. of 2,4,6-tribromophenol is obtained
Hydrogenation	Un-saturation of ring is removed
Reaction with formaldehyde	▪ This is a condensation polymerization of phenol ▪ Formaldehyde polymerizes with phenol produces bakelite. ▪ Bakelite is used for manufacturing of switch buttons









ETHERS

Those organic compounds in which an oxygen atom is bonded to two alkyl groups or aryl groups are called ether.

R-O-R$_1$
R = R$_1$ (symmetrical ethers)
R ≠ R$_1$ (unsymmetrical ethers)

Chapter 11

Alcohols, Phenols & Ethers

NOMENCLATURE

Formula	Common Names	IUPAC
CH_3OCH_3	Dimethyl ether	Methoxy methane
$CH_3OC_2H_5$	Methyl ethyl ether	Methoxy ethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxy ethane
$CH_3OC_6H_5$	Methyl phenyl ether (Anisol)	Methoxy benzene

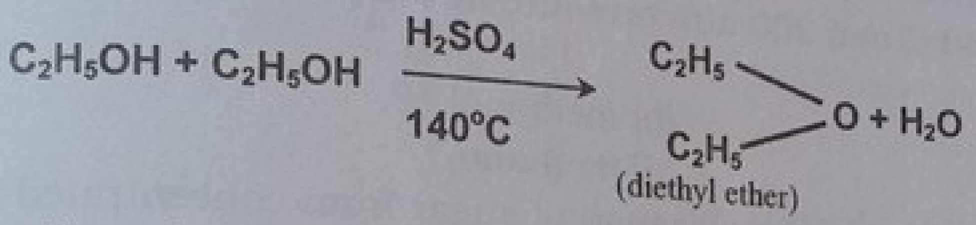
PREPARATION OF ETHER

1. By Williamson's synthesis

$$CH_3CH_2OH + 2Na \longrightarrow 2CH_3CH_2O^-Na^+ + H_2$$

$$C_2H_5ONa + CH_3CH_2Br \longrightarrow \underset{\text{diethyl ether}}{CH_3CH_2OCH_2CH_3} + NaBr$$

2. Condensation of alcohols

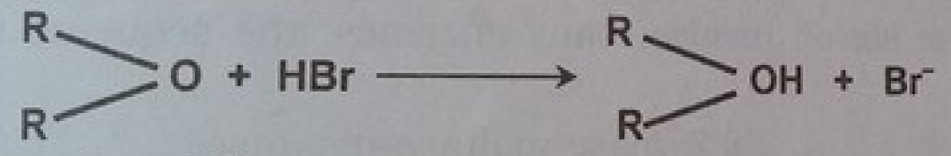


3. Reaction of alkyl halide and Ag_2O

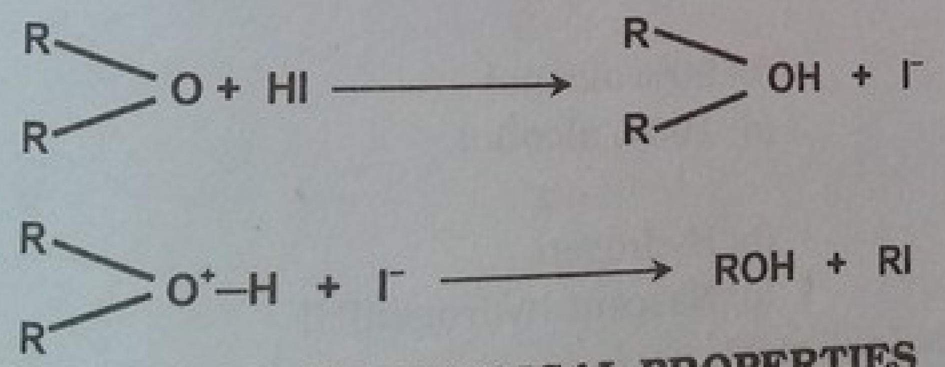
$$2C_2H_5Cl + Ag_2O \xrightarrow{\text{heat}} C_2H_5OC_2H_5 + 2AgCl$$

CHEMICAL REACTIVITY OF ETHER

Reaction with acid



Stronger acid



COMPARISON OF PHYSICAL PROPERTIES

Property	Alcohol	Phenol	Ether
Solubility in water	Soluble	Sparingly soluble at room temperature; soluble at 68.5°C	Slightly soluble
Volatile	Volatile	Almost non volatile	More Volatile
Hydrogen binding	Present	Present	Absent

PRACTICE EXERCISE

20 mins Time Yourself

1. Which one of the following is termed as benzyl alcohol?
(a) C_6H_5OH
(b) $C_6H_5CH(OH)_2$
(c) $C_6H_5CH_2OH$
(d) C_6H_5COOH

2. Which one of the following is also known as lactic acid?
(a) 3-Hydroxy propanoic acid
(b) 2-hydroxy propanoic acid
(c) 2-hydroxy butanoic acid
(d) 3-hydroxy butanoic acid

3. Which one of the following is also known as tartaric acid?
(a) 2,3-dihydroxy butane 1,4-dioic acid
(b) 2,3-dihydroxy butanedioic acid
(c) 2,3-dihydroxy butanoic acid
(d) 2,2-dihydroxy butanoic acid

4. Water gas heated at 450°C and 200 atm pressure in the presence of $ZnO+Cr_2O_3$ will produce
(a) methanal
(b) methanol
(c) carbonic acid
(d) methane

5. The residue obtained after the crystallization of sugar from concentrated sugar cane juice is called
(a) Mother liquor
(b) Filterate
(c) Extract
(d) Molasses

6. The formula of starch is
(a) $C_{12}H_{22}O_{11}$
(b) $C_6H_{10}O_5$
(c) $(C_6H_{10}O_5)_n$
(d) $C_6H_{12}O_6$

7. The process of fermentation of starch involve many enzymes, the sequence of enzymes used are
(a) Diastase-maltase-zymase
(b) Zymase-maltase-diastase
(c) Maltase-diastase-zymase
(d) Diastase-zymase-maltase

8. The rectified spirit contains
(a) 12% alcohol
(b) 90% alcohol
(c) 95% alcohol
(d) 100% alcohol

9. $K_2Cr_2O_7/H_2SO_4$ generate
(a) Oxygen
(b) Hydrogen
(c) Nascent oxygen[O]
(d) Nascent hydrogen[H]

10. The oxidation of isopropyl alcohol will yield
(a) Propane
(b) Propanol
(c) Propanone
(d) Propanoic acid

11. Which alcohol will undergo elimination reaction to give alkene in the presence of acidic potassium dichromate?
(a) Primary alcohol
(b) Secondary alcohol
(c) Tertiary alcohol
(d) All of above

12. The distinction test for primary, secondary, and tertiary alcohol required to react each of them is
(a) Conc. HCl and anhydrous $SOCl_2$
(b) Conc. HCl and anhydrous $CaCl_2$
(c) Conc. HCl and anhydrous PCl_5
(d) Conc. HCl and anhydrous $ZnCl_2$

13. Which compound is also known by the name of carbolic acid?
(a) C_2H_5OH
(b) H_2CO_3
(c) C_6H_5OH
(d) H_3PO_3

14. The given dissociation constant (Ka) value 1.3×10^{-10} is of
(a) Alcohol
(b) Acetic acid
(c) Water
(d) Phenol

15. Heating phenol with Zn will yield
(a) Benzene
(b) Benzoic acid
(c) Phenoxide
(d) Cyclohexane

16. When phenol is heated with concentrated nitric acid, the product is
(a) Picric acid
(b) o-nitrophenol
(c) 1,3,5-trinitro benzene
(d) p-nitrophenol

17. Treating phenol with formaldehyde in the presence of dilute base forms Bakelite. The process involved is
(a) oxidation
(b) elimination
(c) condensation polymerization
(d) additional polymerization

18. Which compound shows hydrogen bonding?
(a) C_2H_6
(b) C_2H_5Cl
(c) CH_3OCH_3
(d) C_2H_5OH

19. Ethanol can be converted into ethanoic acid by
(a) Hydrogenation
(b) Hydration
(c) Oxidation
(d) Fermentation

20. Methyl alcohol is not used
(a) As a solvent
(b) As an antifreezing agent
(c) As a substitute for petrol
(d) For denaturing of ethyl alcohol

21. Methanol can be obtained from
(a) water gas
(b) destructive distillation of wood
(c) methane
(d) all

22. An alcohol which can be prepared by fermentation is
(a) CH_3OH
(b) C_3H_7OH
(c) CH_3-CH_2-OH
(d) C_6H_5OH

23. Absolute alcohol is obtained when rectified spirit is treated with
(a) $Ca(OH)_2$
(b) $CaCO_3$
(c) $CaCl_2$
(d) CaO

24. When alcohol reacts with phosphorous halides it give
(a) alkyl halides
(b) alkyl amine
(c) alkanes
(d) alkynes

25. Phenol was isolated by Runge from
(a) vegetable oil (b) coaltar
(c) wood (d) none of these

26. Which one of the following compound does not have – OH group
(a) ethylene glycol (b) glycerol
(c) picric acid (d) ethyl acetate

27. The hydrogenation of phenol in the presence of Ni and heat gives
(a) cyclohexane (b) n – hexane
(c) 1 – hexanol (d) cyclohexanol

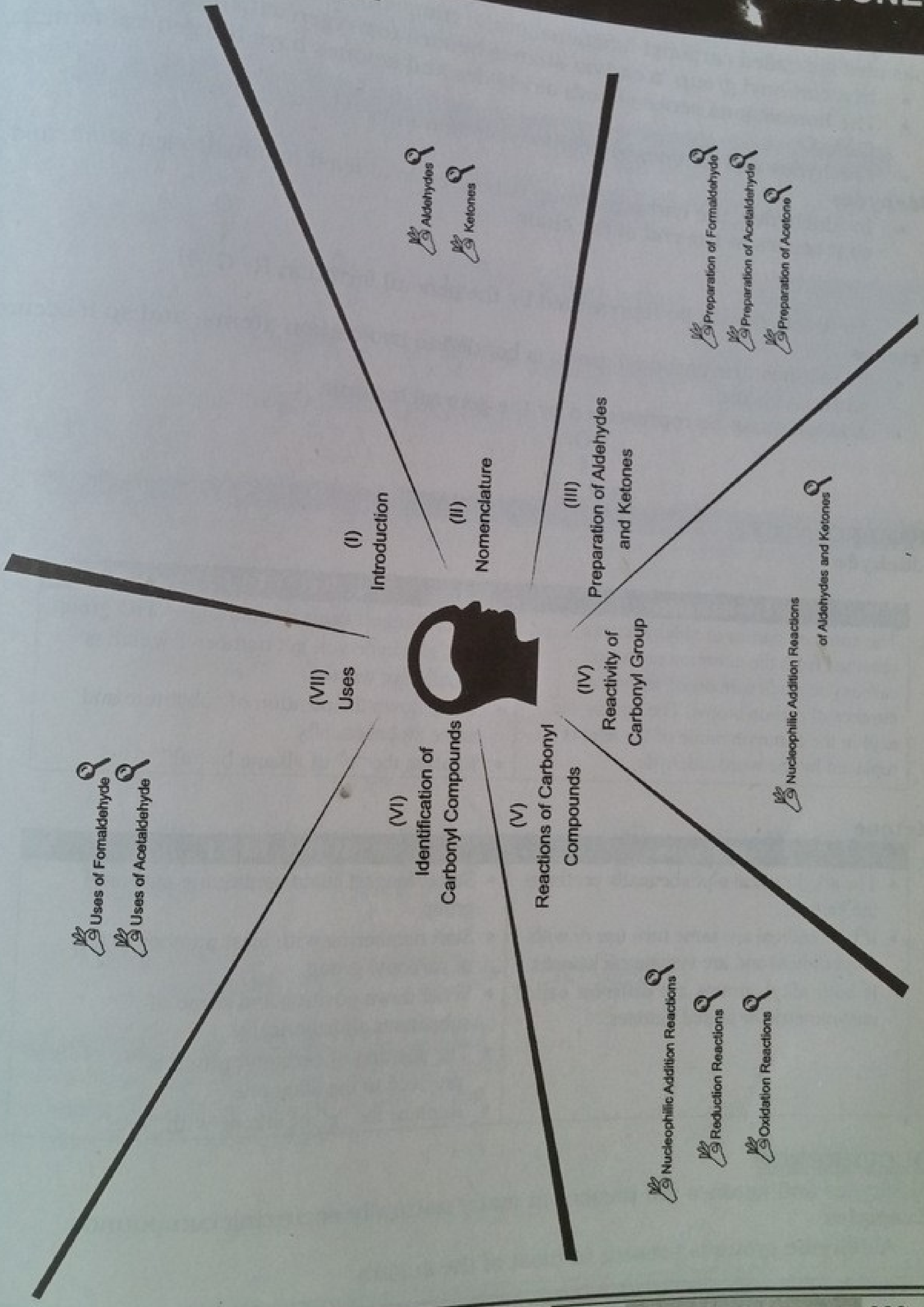
28. Ethers show functional group isomerism with
(a) aldehydes (b) ketones.
(c) alcohols (d) carboxylic acid

29. Ethanol and methanol can be distinguished by a
(a) Iodoform test (b) Lucas test
(c) Benedicts' test (d) Tollen's test

30. Which one of the following alcohol has greater boiling point
(a) ethanol (b) ethylene glycol
(c) glycerol (d) methanol

Chapter 12

ALDEHYDES AND KETONES


(I) Introduction
Aldehydes
Ketones
(II) Nomenclature
(III) Preparation of Aldehydes and Ketones
Preparation of Formaldehyde
Preparation of Acetaldehyde
Preparation of Acetone
(IV) Reactivity of Carbonyl Group
Nucleophilic Addition Reactions of Aldehydes and Ketones
(V) Reactions of Carbonyl Compounds
Nucleophilic Addition Reactions
Reduction Reactions
Oxidation Reactions
(VI) Identification of Carbonyl Compounds
(VII) Uses
Uses of Fomaldehyde
Uses of Acetaldehyde

Chapter 12 Aldehydes & Ketones

CARBONYL COMPOUNDS

The organic compounds which contain carbonyl functional group $[-\overset{\overset{O}{\|}}{C}-]$ in their molecules are called carbonyl functional group compounds.

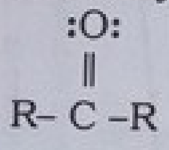
- In a carbonyl group, a carbon atom is bonded to oxygen with a double bond
- The homologous series of both aldehydes and ketones have the general formula $C_nH_{2n}O$
- Aldehydes and Ketones are carbonyl compounds

Aldehydes

- In Aldehydes, the carbonyl group is bonded to at least one hydrogen atom, and so it occurs at the end of the chain.
- An Aldehyde can be represented by the general formula, $R-\overset{\overset{O}{\|}}{C}-H$

Ketones

- In Ketones, the carbonyl group is bonded to two carbon atoms, and so it occurs within a chain.
- A ketone may be represented by the general formula



$$R-\overset{\overset{:O:}{\|}}{C}-R$$

NOMENCLATURE

Aldehyde

Trivial name	IUPAC RULE
The common names of aldehydes are obtained from the common names of carboxylic acids containing the same number of carbon atoms. The ending –ic acid in the common name of the acid is replaced by the word aldehyde.	• Select longest chain containing –CHO group • C of aldehyde will get number 1 which is usually not written • Write down the position of substitute and name alphabetically • Replace the "e" of alkane by "al"

Ketone

Trivial name	IUPAC RULE
• The alkyl radical alphabetically prefix to the ketone. • If both radical are same then use di with alkyl radical and are symmetric ketones. • If both alkyl groups are different called unsymmetric or mixed ketones.	• Select longest chain containing carbonyl group • Start numbering with least number to C of carbonyl group. • Write down position and name of substitutes alphabetically • The position of carbonyl group is prefixed to the alkanone • Replace the "e" of alkane with "one"

OCCURRENCE

Aldehydes and ketones are present in many naturally occurring compounds.

Examples

- **Aldehydic** group is present in most of the sugars

Chapter 12

Aldehydes & Ketones

- Aldehydes are principle constituents of a number of essential oils used as fragrances and flavours.
- The **ketonic** group is present in camphor and menthone

PREPARATION OF ALDEHYDES

Formaldehyde

Industrial method	Laboratory method
By passing methanol vapours and air over iron oxide-molybdenum oxide or silver catalyst at 500° C	By passing methanol vapours and air over platinised asbestos or copper or silver catalyst at 300°C

- Laboratory Method

$$2CH_3OH + O_2 \xrightarrow[300°C]{\text{Pt-asbestos}} 2HCHO + 2H_2O$$

- Industrial Method

$$2CH_3OH + O_2 \xrightarrow[\text{FeO, MoO}_3]{500°C} 2HCHO + 2H_2O$$

$$(HCOO)_2Ca \xrightarrow{\Delta} HCHO + CaCO_3$$

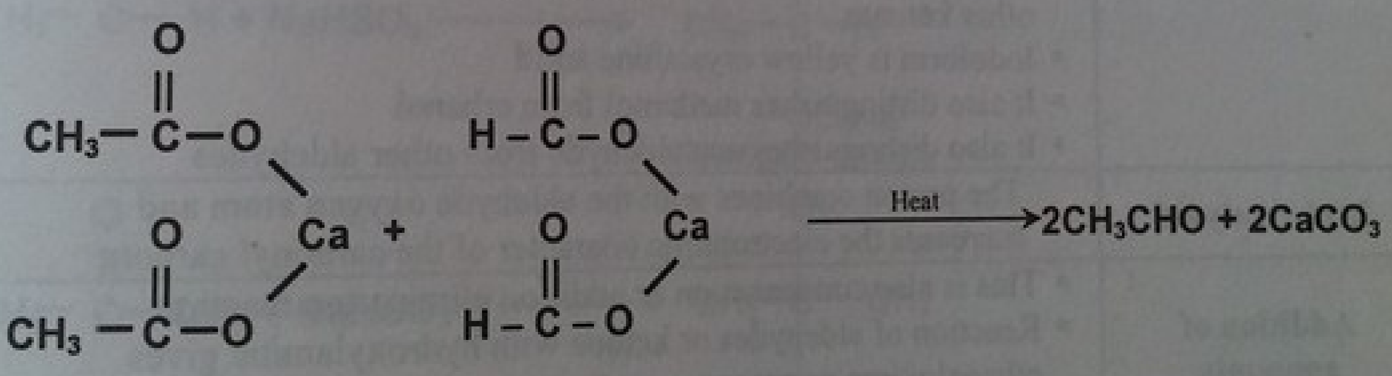
Formalin
A mixture of 40% formaldehyde, 8% methyl alcohol and 52% water

Acetaldehyde

Laboratory method	Industrial method
▪ By oxidation of ethyl alcohol with acidified sodium dichromate ▪ By dry distillation of mixture of calcium salt of formic acid and acetic acid	By oxidation of ethylene using palladium chloride catalyst with cupric chloride as promoter

- Laboratory Method

$$2CH_3CH_2OH + [O] \xrightarrow[Na_2Cr_2O_7 + H_2SO_4]{\Delta} 2CH_3CHO + 2H_2O$$

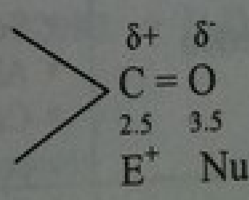


- Industrial Method

$$2CH_2{=}CH_2 + O_2 \xrightarrow[H_2O]{PdCl_2 + CuCl_2} 2CH_3CHO$$

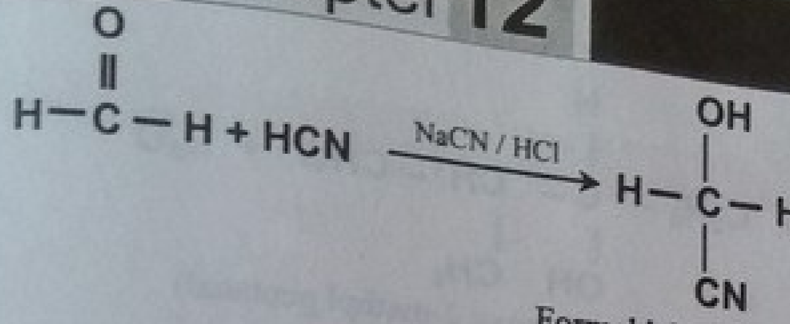
REACTIVITY OF CARBONYL GROUP

Both carbon and oxygen are sp^2 hybridized
Reactivity of carbonyl group is due to the polarity of carbon and oxygen. $\overset{\delta+}{C}=\overset{\delta-}{O}$



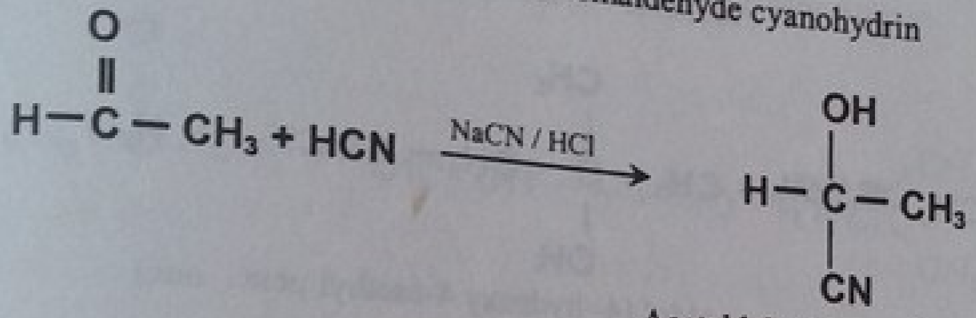
REACTION OF CARBONYL COMPOUNDS

Detail of reaction	Remarks
Base catalyzed reaction mechanism	▪ This reaction will take place with strong nucleophilic reagent ▪ Base reacts with reagent and releases nucleophile
Addition of hydrogen cyanide	▪ Compound produced called cyanohydrins. ▪ On reaction with aqueous acid, cyanohydrin changes into carboxylic acid ▪ This reaction is used for the synthesis of α-hydroxy acid
Addition of Grignard's reagent	Grignard reagents add to aldehydes and ketones to form adducts which on hydrolysis with a dilute mineral acid (HCl, H_2SO_4) give alcohols.
Addition of sodium bisulphite	▪ White ppt. of sodium bisulphite product is produced ▪ On heating, bisulphite product again regenerates into aldehyde or ketone ▪ This reaction is used to separate carbonyl compound from non carbonyl compounds such as alcohols.
Aldol condensation reaction	▪ The reaction in which, two aldehydes, two ketones and aldehyde and ketones react in presence of base to give α hydroxy aldehyde or ketone is called adol condensation ▪ Mechanism involve carbanion
Cannizzaro's reaction	▪ It is a self oxidation reduction reaction ▪ Oxidized product is salt of an acid ▪ Reduced product is alcohol ▪ Reaction is carried at 50% NaOH ethanol at room temperature.
Haloform reaction	▪ Acetaldehyde, ethanol, methyl ketones and isopropyl alcohol undergo such reaction ▪ This reaction is used to distinguish between methyl ketone from other ketones ▪ Iodoform is yellow crystalline solid ▪ It also distinguishes methanol from ethanol ▪ It also distinguishes acetaldehyde from other aldehydes
Acid catalysed	The proton combines with the aldehyde oxygen atom and increases the electrophilic character of the carbonyl carbon.
Addition of ammonia derivative	▪ This is also condensation or addition elimination reaction ▪ Reaction of aldehydes or ketone with hydroxylamine gives ethanaloxime or propanoneoxime ▪ On reaction with phenylhydrazine carbonyl compounds give phenyl-hydrazone
Reduction	▪ Hydrogenation of aldehyde gives primary alcohol and that of ketone gives secondary alcohol. ▪ Sodium tetrahydroborate is source of H^- ▪ Alkoxide formation occurs. ▪ Catalytic reduction is carried out in the presence of Pd, Pt, Ni and products remained same
Addition of alcohol	▪ Acetal is produced on reaction of carbonyl with alcohol but ketones do not react under these conditions. ▪ This reaction is also used in protection of aldehyde group.



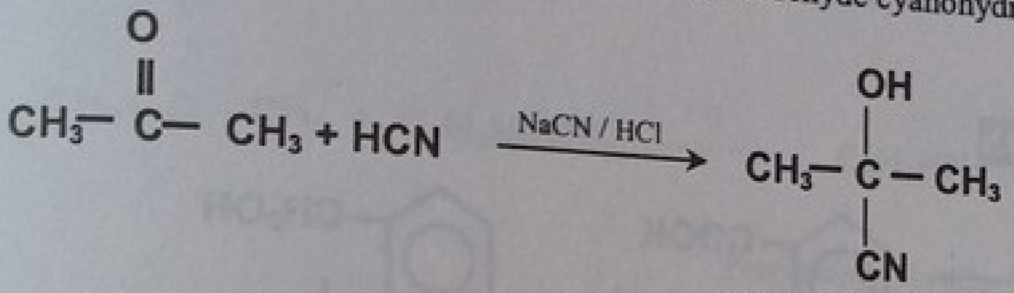
$$\mathrm{H-\overset{\overset{O}{\|}}{C}-H + HCN \xrightarrow{NaCN\,/\,HCl} H-\underset{\underset{CN}{|}}{\overset{\overset{OH}{|}}{C}}-H}$$

Formaldehyde cyanohydrin



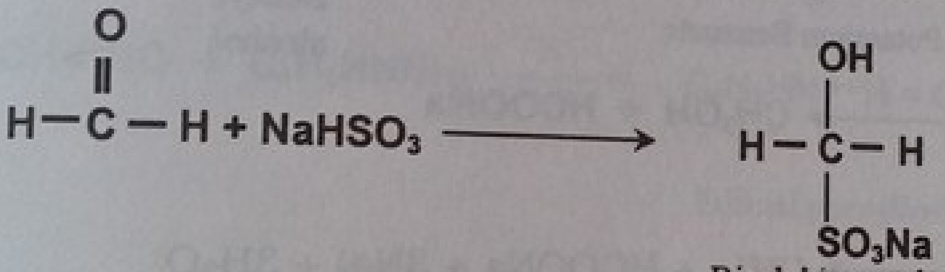
$$\mathrm{H-\overset{\overset{O}{\|}}{C}-CH_3 + HCN \xrightarrow{NaCN\,/\,HCl} H-\underset{\underset{CN}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3}$$

Acetaldehyde cyanohydrin



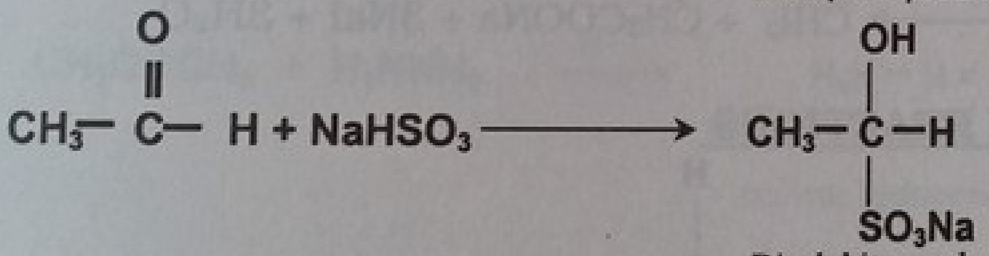
$$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + HCN \xrightarrow{NaCN\,/\,HCl} CH_3-\underset{\underset{CN}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3}$$

Acetone cyanohydrin



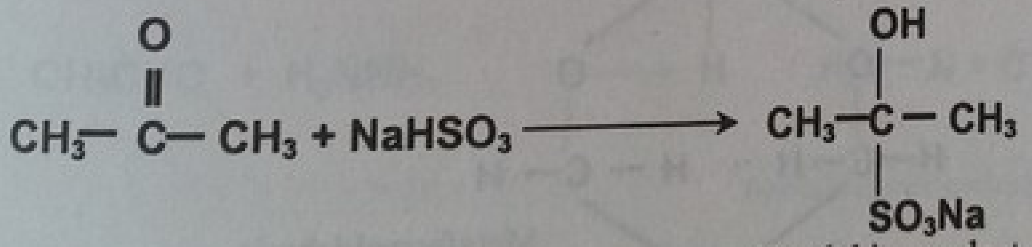
$$\mathrm{H-\overset{\overset{O}{\|}}{C}-H + NaHSO_3 \longrightarrow H-\underset{\underset{SO_3Na}{|}}{\overset{\overset{OH}{|}}{C}}-H}$$

Bisulphite product



$$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-H + NaHSO_3 \longrightarrow CH_3-\underset{\underset{SO_3Na}{|}}{\overset{\overset{OH}{|}}{C}}-H}$$

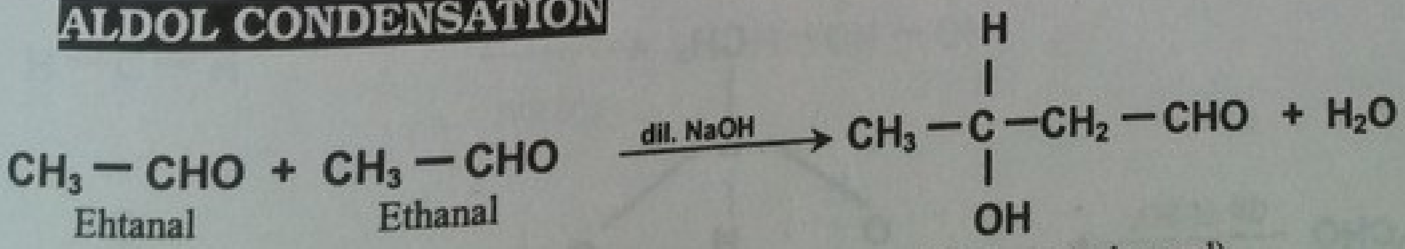
Bisulphite product



$$\mathrm{CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + NaHSO_3 \longrightarrow CH_3-\underset{\underset{SO_3Na}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3}$$

Bisulphite product

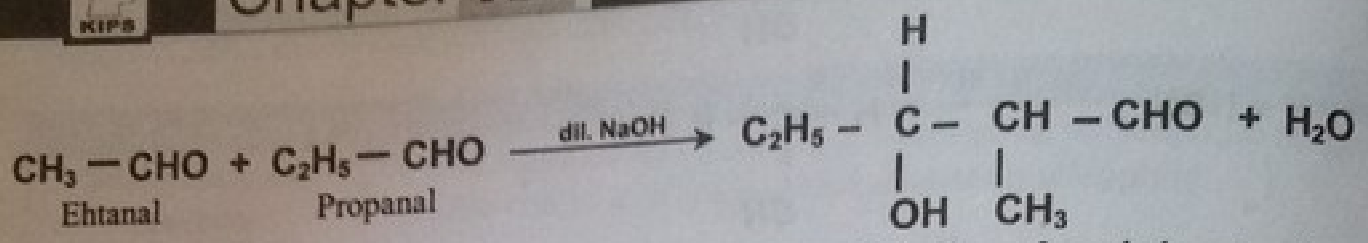
ALDOL CONDENSATION



$$\mathrm{CH_3-CHO + CH_3-CHO \xrightarrow{dil.\ NaOH} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-CH_2-CHO + H_2O}$$

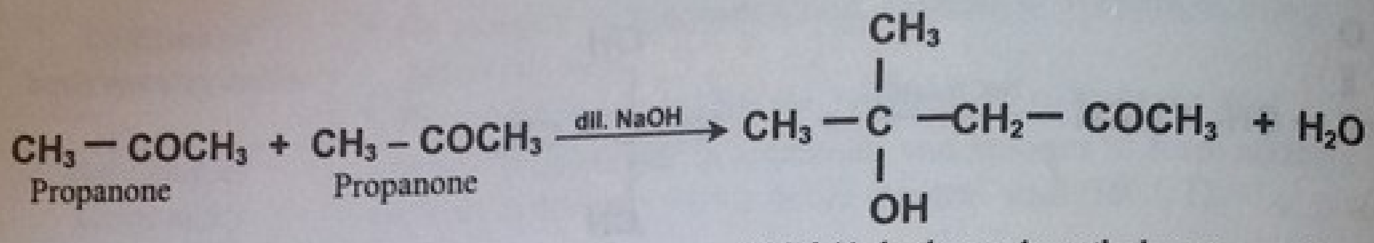
Ehtanal Ethanal

Aldol (3- hydroxy butanal)



$$CH_3-CHO + C_2H_5-CHO \xrightarrow{\text{dil. NaOH}} C_2H_5-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-\underset{\displaystyle CH_3}{CH}-CHO + H_2O$$

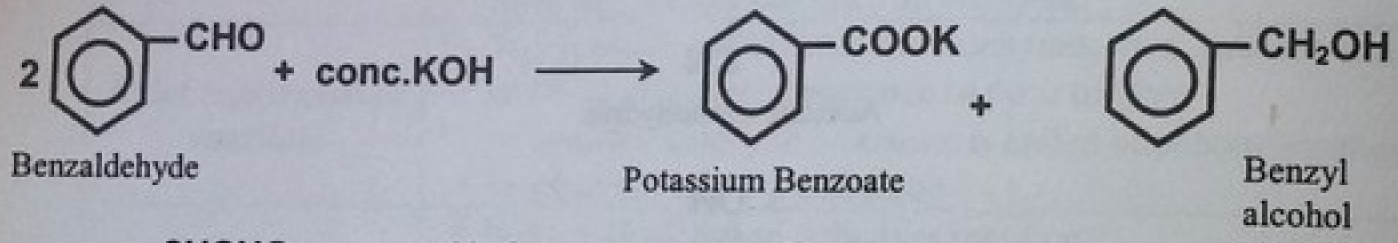
Adduct (3- hydroxy 2-methyl pentanal)



$$CH_3-COCH_3 + CH_3-COCH_3 \xrightarrow{\text{dil. NaOH}} CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}-CH_2-COCH_3 + H_2O$$

Aldol (4- hydroxy 4-methyl pentanone)

CANNIZZARO REACTION



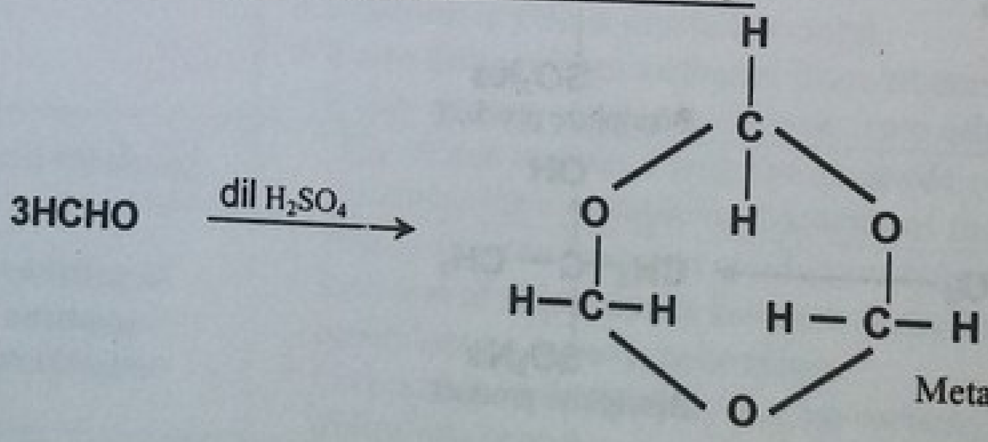
$2HCHO + \text{conc.}NaOH \longrightarrow CH_3OH + HCOONa$

HALOFORM REACTION

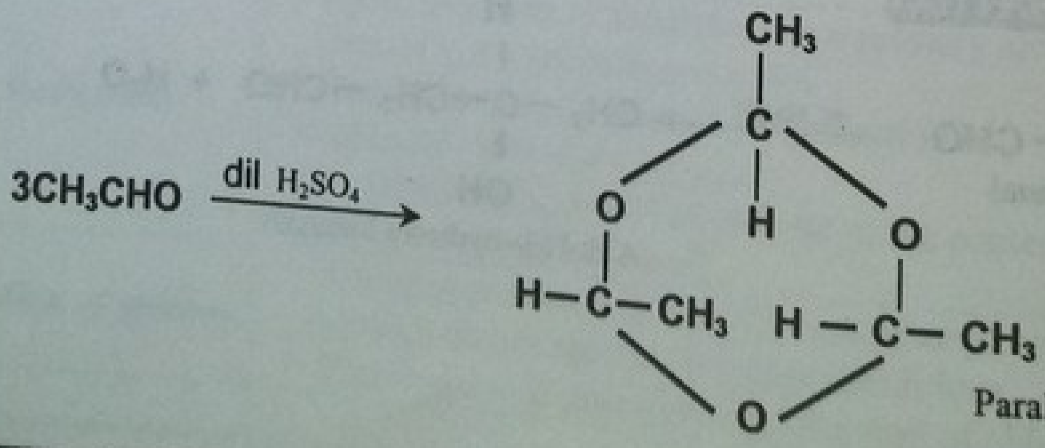
$CH_3CHO + 3I_2 + 4NaOH \longrightarrow CHI_3 + HCOONa + 3NaI + 3H_2O$

$CH_3OCH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3 + CH_3COONa + 3NaI + 3H_2O$

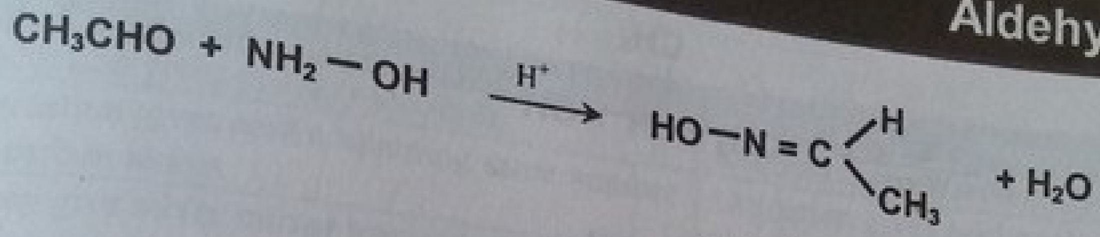
ACID CATALYZED ADDITION REACTIONS



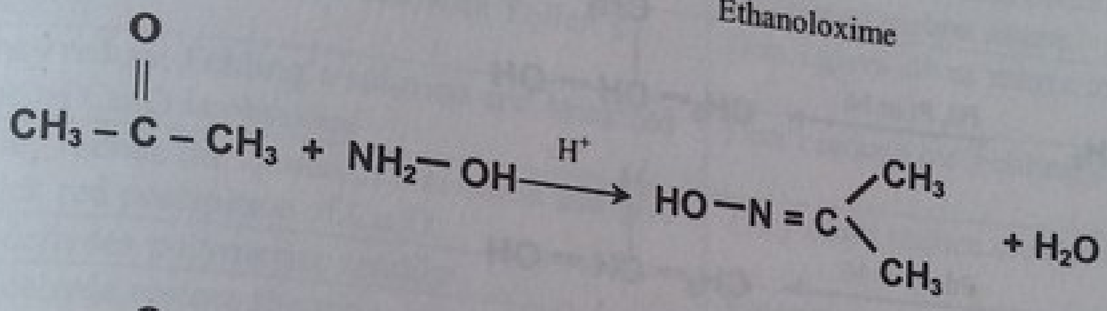
Metaformaldehyde



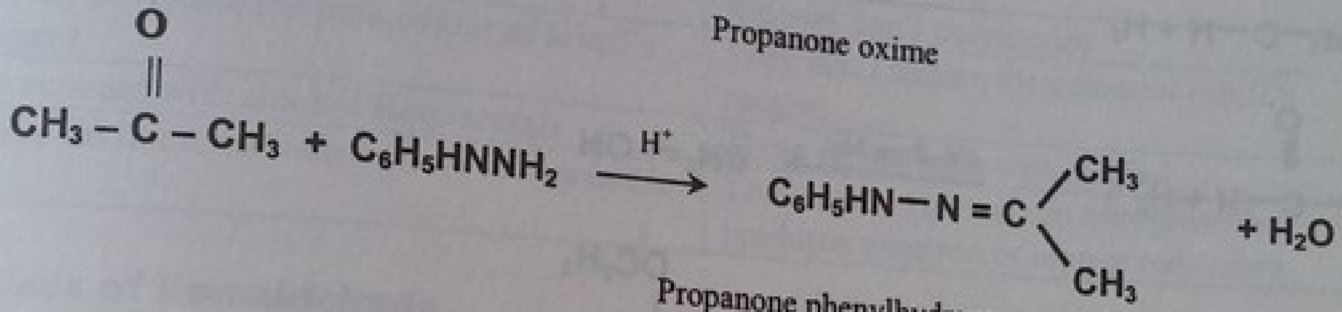
Paraldehyde



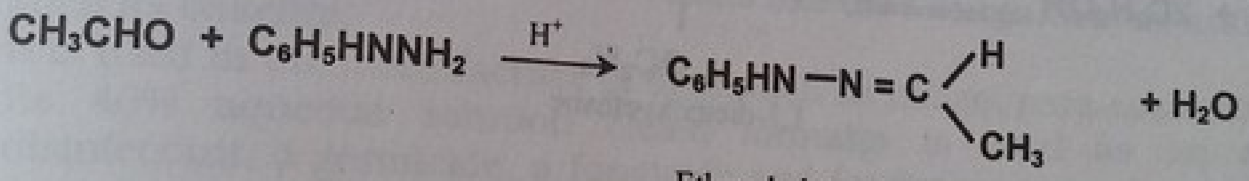
Ethanoloxime



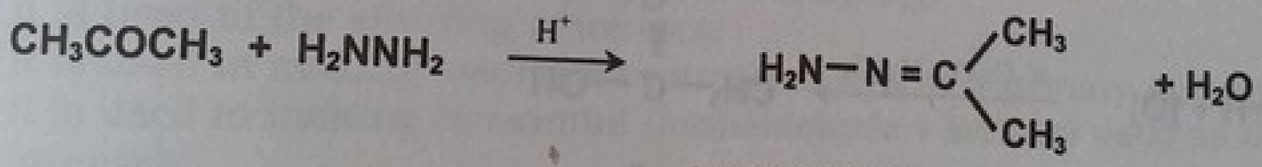
Propanone oxime



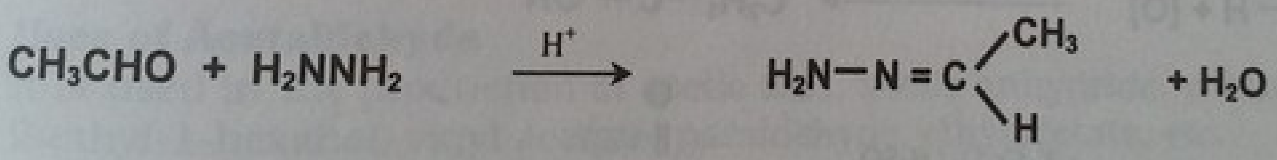
Propanone phenylhydrazone



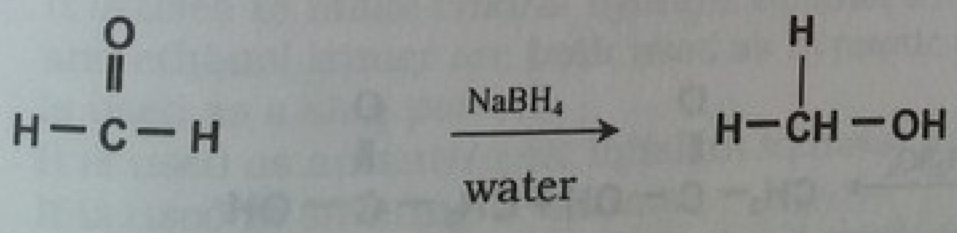
Ethanal phenylhydrazone



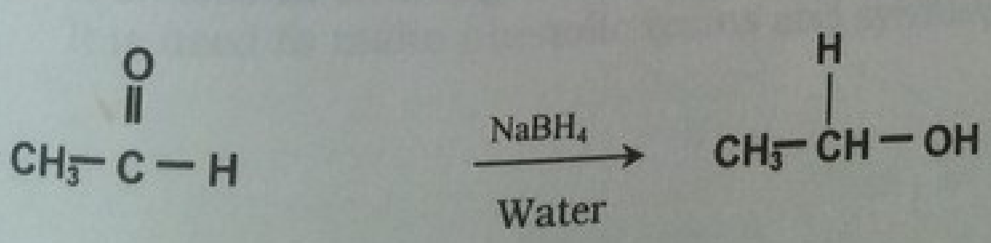
Acetone hydrazone



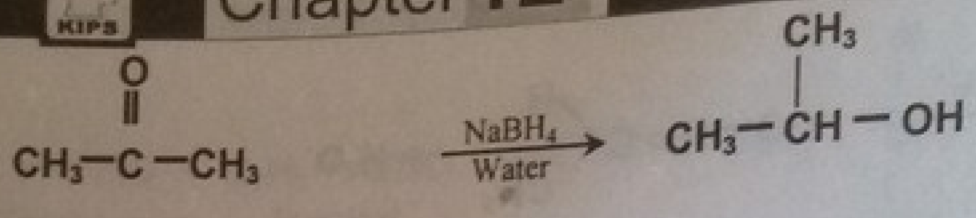
Acetaldehyde hydrazone



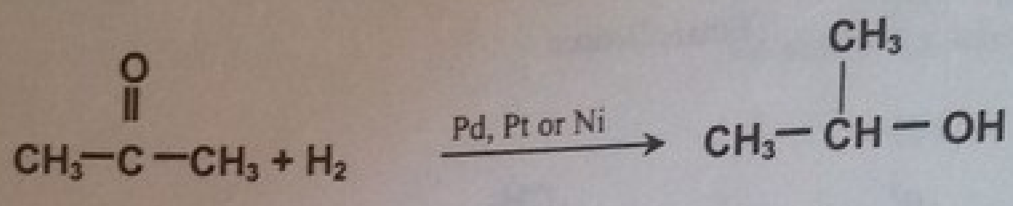
$$H-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow[\text{water}]{NaBH_4} H-\overset{\overset{\displaystyle H}{|}}{C}H-OH$$



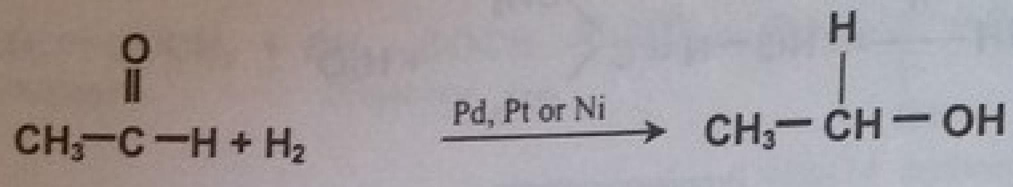
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H \xrightarrow[\text{Water}]{NaBH_4} CH_3-\overset{\overset{\displaystyle H}{|}}{C}H-OH$$



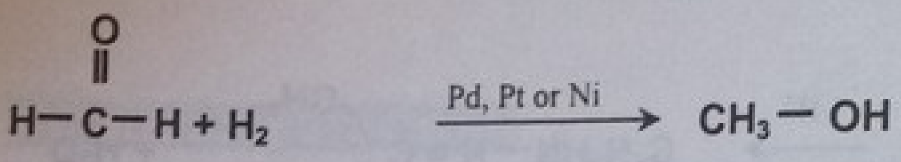
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[\text{Water}]{NaBH_4} CH_3-\underset{}{\overset{\overset{\displaystyle CH_3}{|}}{C}H}-OH$$



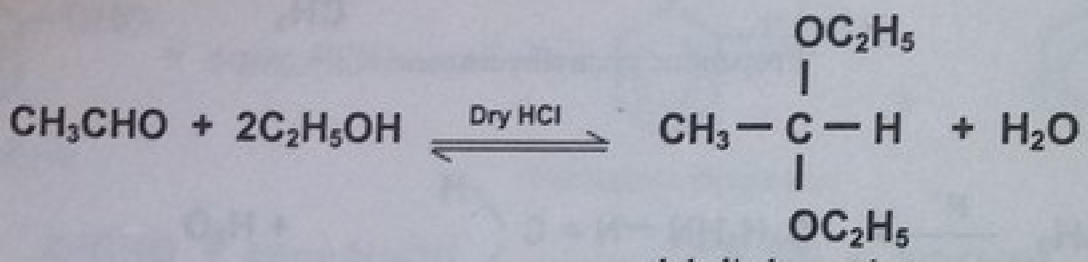
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + H_2 \xrightarrow{\text{Pd, Pt or Ni}} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-OH$$



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + H_2 \xrightarrow{\text{Pd, Pt or Ni}} CH_3-\overset{\overset{\displaystyle H}{|}}{C}H-OH$$



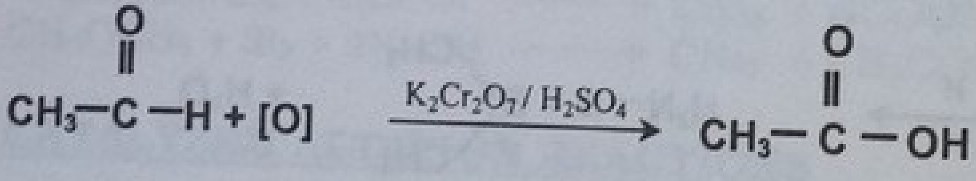
$$H-\overset{\overset{\displaystyle O}{\|}}{C}-H + H_2 \xrightarrow{\text{Pd, Pt or Ni}} CH_3-OH$$



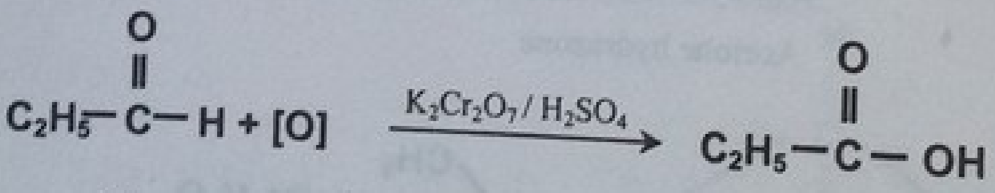
$$CH_3CHO + 2C_2H_5OH \underset{}{\overset{\text{Dry HCl}}{\rightleftharpoons}} CH_3-\underset{\underset{\displaystyle OC_2H_5}{|}}{\overset{\overset{\displaystyle OC_2H_5}{|}}{C}}-H + H_2O$$

1,1-diethoxyethane

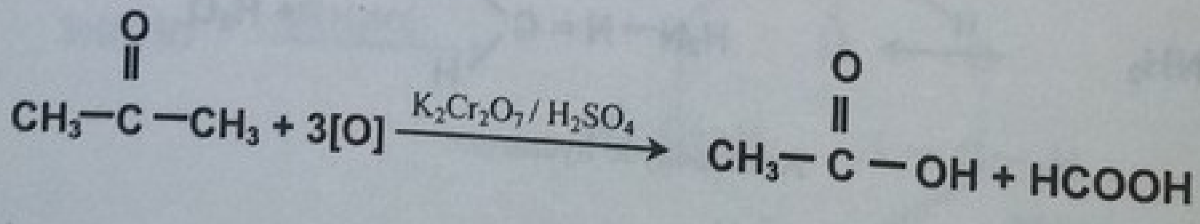
OXIDATION



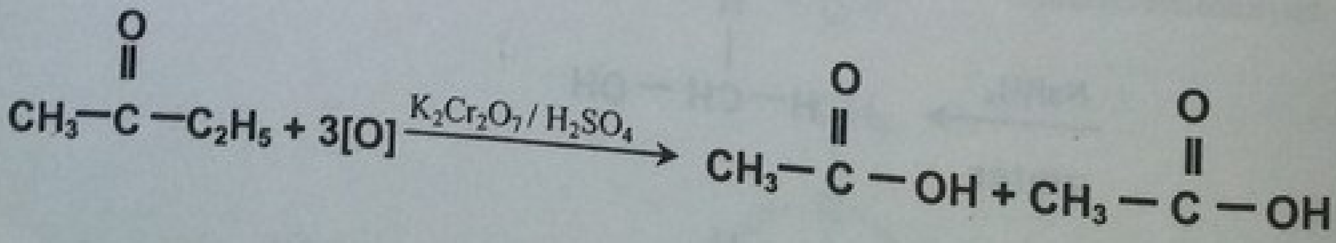
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + [O] \xrightarrow{K_2Cr_2O_7/\,H_2SO_4} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$



$$C_2H_5-\overset{\overset{\displaystyle O}{\|}}{C}-H + [O] \xrightarrow{K_2Cr_2O_7/\,H_2SO_4} C_2H_5-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + 3[O] \xrightarrow{K_2Cr_2O_7/\,H_2SO_4} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + HCOOH$$



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-C_2H_5 + 3[O] \xrightarrow{K_2Cr_2O_7/\,H_2SO_4} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

IDENTIFICATION OF CARBONYL COMPOUNDS

Aldehydes	Ketones
Reduction gives primary alcohols	Reduction gives secondary alcohols
Oxidation gives acid containing same number of carbon atoms	Oxidation gives acid containing smaller number of carbon atoms
They give silver mirror test with Tollen's reagent	Don't gives silver mirror test
They reduce Fehling's solution and brick red ppt. of Cu_2O is obtained	Don't reduce the Fehling's solution
They reduce the Benedict's solution and give brick red precipitate of Cu_2O	They don't reduce the Benedict's solution
Aldehydes polymerize readily	Ketones don't polymerize
Aldehyde restore the pink colour of schiff's reagent	They don't restore the colour of schiff's reagent
These react with alcohol form acetals	These do not react with alcohol
These do not react with sodium nitroprusside	These react with sodium nitroprusside produces wine red or orange red colour

(a) **Uses of Fomaldehyde**

(i) It is used in the manufacture of resins like urea-formaldehyde and plastics such as bakelite.

(ii) It is used in the manufacture of dyes such as indigo, para-rosaniline, etc

(iii) Its 40% aqueous solution called formalin is used as an antiseptic, disinfectant, a germicide, a fungicide and for preserving animal specimens a sterlising surgical instruments.

(iv) It is used as a decolourising agent in vat dyeing.

(v) It is used in the silvering of mirrors.

(vi) It is used in making medicine urotropine used as a urinary antiseptic

(vii) It is used in making formamint (formaldehyde + lactose) used as throat lozenges.

(viii) It is used in the processing of anti-poliovaccine.

(b) **Uses of Acetaldehyde**

(i) It is used in the production of acetic acid, acetic anhydride, n-butanol, ethar 2-ethyl-1-hexanol, vinyl acetate, paraldehyde, ethylacetate, etc.

(ii) It is used to make acetaldehyde ammonia used as a rubber-accelerator.

(iii) It is used to make chloral hydrate, ethanol trimer and tetramer. Chloral hydr and ethanol trimer are both used as hypnotic drugs whereas ethanol tetrame is used as a slug poison.

(iv) It is used as an antiseptic inhalant in nasal infections.

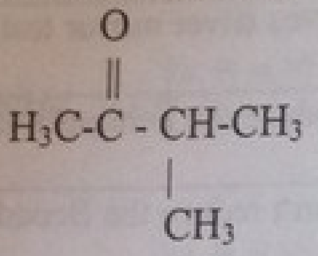
(v) It is used in silvering of mirrors.

(vi) It is used to make phenolic resins and synthetic drugs.

PRACTICE EXERCISE

30 mins
Time Yourself

1. Trivial name of the following compound is



$$H_3C-\overset{\overset{\large O}{\|}}{C}-\underset{\underset{\large CH_3}{|}}{CH}-CH_3$$

(a) Methyl-n propyl ketone
(b) Dimethyl ethyl ketone
(c) Methyl neo-propyl ketone
(d) Methyl isopropyl ketone

2. Which of the following substance produce acetaldehyde on dry distillation?
(a) $(CH_3COO)_2Ca$
(b) $(HCOO)_2Ca$
(c) both (a) and (b)
(d) none

3. Which of the following will have the highest boiling point?
(a) methanal
(b) ethanal
(c) propanal
(d) hexanone

4. Which of the following reaction is not shown by ketones?
(a) reaction with HCN
(b) reaction with $NaHSO_3$
(c) reaction with 2,4 dinitrophenyl hydrazine
(d) reaction with Fehling solution

5. The carbon atom of carbonyl group is
(a) sp hybridized
(b) sp^2 hybridized
(c) sp^3 hybridized
(d) dsp^2 hybridized

6. Which of the following substances does not give iodoform test?
(a) acetaldehyde
(b) ethyl alcohol
(c) methyl alcohol
(d) acetone

7. Formalin is ________% solution of formaldehyde in water
(a) 10%
(b) 20%
(c) 40%
(d) 60%

8. Which of the following aldehydes shows rapid reaction with sodium nitroprusside?
(a) formaldehyde
(b) acetaldehyde
(c) benzaldehyde
(d) acetone

Acetone reacts with HCN to form a cyanohydrin. It is an example of
(a) electrophilic addition
(b) electrophilic substitution
(c) nucleophilic addition
(d) nucleophilic substitution

0. Consider the following reaction.

$$CH_3COCH_3 + 4[O] \xrightarrow{K_2Cr_2O_7\ conc.\ H_2SO_4}$$

Which of the following product is formed?
(a) CH_3OH
(b) CH_3-CH_2-OH
(c) $CH_3COOH+HCOOH$
(d) Reaction is not possible

Which of the following compounds will react with Tollen's reagent?
(a) $CH_3.CHO$
(b) $CH_3-CO-CH_3$
(c) CH_3-COOH
(d) $CH_3-CO-CH_2-CH_3$

12. Which of the following reactions may be associated with aldehyde and ketone?
(a) nucleophile addition (b) polymerization
(c) oxidation (d) all of the above

13. Cannizzaro's reaction is not given by
(a) formaldehyde (b) acetaldehyde
(c) benzaldehyde (d) trimethyl acetaldehyde

14. Which of the following reagents will react with both aldehydes and ketones?
(a) Grignard reagent (b) Tollen's reagent
(c) Fehling's reagent (d) Benedict's reagent

15. Ketones are comparatively less reactive than aldehdye. It is due to
(a) alkyl groups are electron donating (b) steric hindrance
(c) both (a) & (b) (d) none

16. Which of the following do not give aldol condensation reactions?
(a) formaldehyde (b) acetaldehyde
(c) diemthyl ketone (d) propionaldehyde

17. Which of the following is not a use of formaldehyde?
(a) in silvery mirror (b) in making medicine urotropine
(c) in making throat lozenges (d) in making acetic acid

18. Formaldehyde and lactose are combined to produce throat lozenges named as
(a) formamint (b) lactomint
(c) aldomint (d) formalactose

19. Which of the following is not a use of acetaldehyde?
(a) formation of phenolic resins (b) formation of mirror
(c) antiseptic inhalant (d) formation of throat lozenges

20. Formula of haloform is
(a) HCOX (b) CX_4
(c) CHX_3 (d) CH_3X

21. Formaldehyde condenses with phenol in the presence of dilute H_2SO_4 to yield
(a) Nylon 66 (b) urotropine
(c) Aniline formaldehyde plastic (d) Bakelite

22. Formalin consists of mixture of formaldehyde, methyl alcohol and water. Percentage of water in it is
(a) 60% (b) 50%
(c) 52% (d) 8%

23. Which of the following will not give addition reaction with $NaHSO_3$
(a) HCHO (b) CH_3CHO
(c) CH_3-CH_2-CHO (d) None of the above

24. On heating aldehydes with Fehling's solution, we get a precipitate whose colour is
(a) pink (b) black
(c) yellow (d) brick red

25. Which of the following compounds has the empirical formula CH_2O and reacts with sodium hydroxide?
(a) carbonic acid (b) ethanol
(c) acetic acid (d) methanoic acid

26. Aldehyde and ketone have same general formula for homologous series
(a) $C_n H_{2n}O_{2n}$ (b) C_nH_{2n}
(c) $C_nH_{2n}O$ (d) $C_nH_{2n}O_{n+1}$

27. Oxidation of primary alcohol gives
(a) Ketone (b) Aldehyde
(c) Alkene then –COOH (d) Ester

28. Ethanal is prepared industrially by air oxidation of ethylene using palladium chloride as catalyst and ______ as promoter
(a) $PdCl_2$ (b) Cu_2Cl_2
(c) $CuCl_2$ (d) $PbCl_2$

29. Nucleophilic addition reactions are catalysed
(a) Acid (b) Base
(c) Both a and b (d) None

30. Acetaldehyele cyanohydrin on acid hydrolysis yields
(a) Tartaric acid (b) Propanoic acid
(c) Lactic acid (d) Valeric acid

31. Acetal on acid hydrolysis generates
(a) Alcohol (b) Ketone
(c) Both a & b (d) None of the above

32. Which one exhibits aldol condensation
(a) HCHO (b) C_6H_5CHO
(c) Cl_3CCHO (d) CH_3COCH_3

33. For aldol condensation the conditions necessary
(a) α-C (b) α-H
(c) Basic medium (d) All

34. Aldehydes are reduced to
(a) P° alcohol (b) S° alcohol
(c) T° alcohol (d) Not possible

35. Tetrahydroborate ion is the source of
(a) proton (b) H^+
(c) both a & b (d) H^-

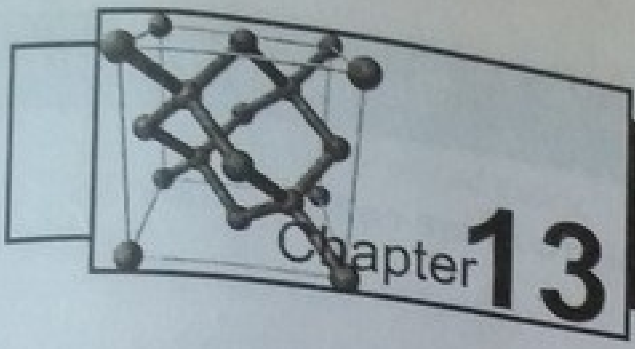
36. Which of the following is a symmetrical ketone
(a) 3- hexanone (b) acetone
(c) butanone (d) 2- pentanone

37. Dry distillation of calcium acetate results in the formation of
(a) formaldehyde (b) acetaldehyde
(c) methane (d) acetone

38. In base catalyzed reaction of carbonyl compound the catalyst
(a) increases the nucleophilic character of reagent
(b) increases electrophilic character of carbonyl compound
(c) acidic character of reagent
(d) both a and b

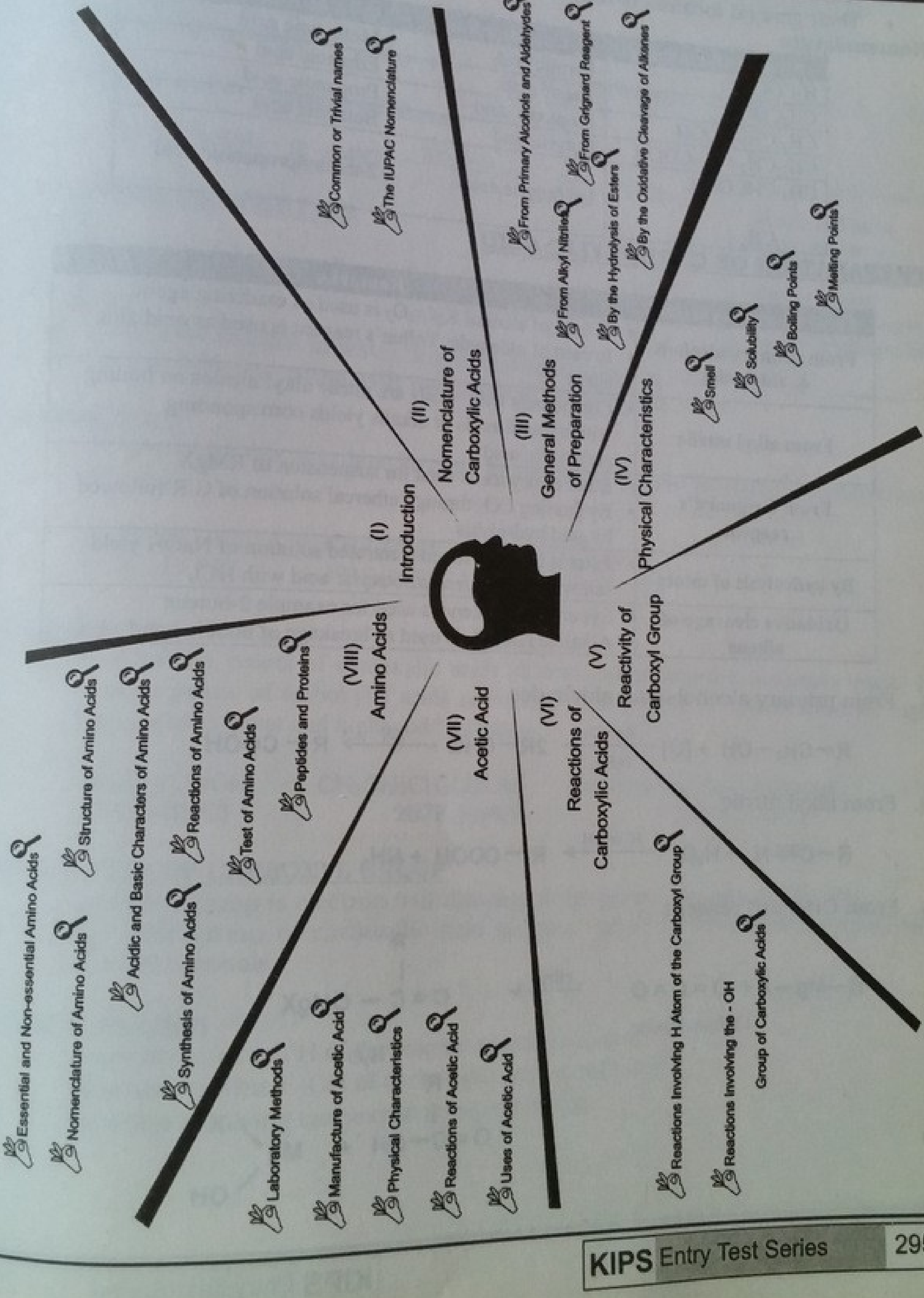
39. Cannizaro's reaction takes place through the transfer of ____ from complex anion.
(a) hydrogen ion (b) hydride ion
(c) oxide ion (d) methoxide ion

40. Iodoform test can be used to distinguish between
(a) ethanol and methanol (b) acetaldehyde and methanal
(c) acetone and diethyl ketone (d) all of the above



Chapter 13

CARBOXYLIC ACIDS


(I) Introduction
(II) Nomenclature of Carboxylic Acids
Common or Trivial names
The IUPAC Nomenclature
(III) General Methods of Preparation
From Primary Alcohols and Aldehydes
From Alkyl Nitriles
From Grignard Reagent
By the Hydrolysis of Esters
By the Oxidative Cleavage of Alkenes
(IV) Physical Characteristics
Smell
Solubility
Boiling Points
Melting Points
(V) Reactivity of Carboxyl Group
(VI) Reactions of Carboxylic Acids
Reactions Involving H Atom of the Carboxyl Group
Reactions Involving the - OH Group of Carboxylic Acids
(VII) Acetic Acid
Laboratory Methods
Manufacture of Acetic Acid
Physical Characteristics
Reactions of Acetic Acid
Uses of Acetic Acid
(VIII) Amino Acids
Essential and Non-essential Amino Acids
Nomenclature of Amino Acids
Structure of Amino Acids
Acidic and Basic Characters of Amino Acids
Synthesis of Amino Acids
Reactions of Amino Acids
Test of Amino Acids
Peptides and Proteins

Chapter 13

CARBOXYLIC ACIDS

Organic compounds containing –COOH as a functional group are called carboxylic acids. (Carb from carbonyl and oxyl from hydroxyl.

- Their general formula is R-COOH

Nomenclature

Structural Formula	Common Name	IUPAC Name
H-COOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3-CH_2-COOH	Propionic acid	Propanoic acid
$CH_3-CH_2-CH_2-COOH$	Butyric acid	Butanoic acid
$CH_3-\underset{\underset{CH_3}{\vert}}{C}HCOOH$	Iso-butyric acid	2-methylpropanoic acid

PREPARATION OF CARBOXYLIC ACID

Description of reaction	Remarks
From primary alcohols & aldehydes	- In case of alcohol $K_2Cr_2O_7$ is used as oxidizing agent. - In case of aldehyde, Tollen's reagent is used as oxidizing agent
From alkyl nitrile	- Compounds with –C≡N are nitrile alkyl nitriles on boiling with mineral acids or alkalis yields corresponding carboxylic acid.
From Grignard's reagent	- Ether or dry ice is used for suspension of RMgX - By passing CO_2 through ethereal solution of G.R followed by acid hydrolysis
By hydrolysis of esters	- Ester is boiled with concentrated solution of NaOH yield salt which gives free carboxylic acid with HCl.
Oxidative cleavage of alkene	- Symmetrical alkene is used for example 2-butene - Alkaline $KMnO_4$ is used as breakage of double bond

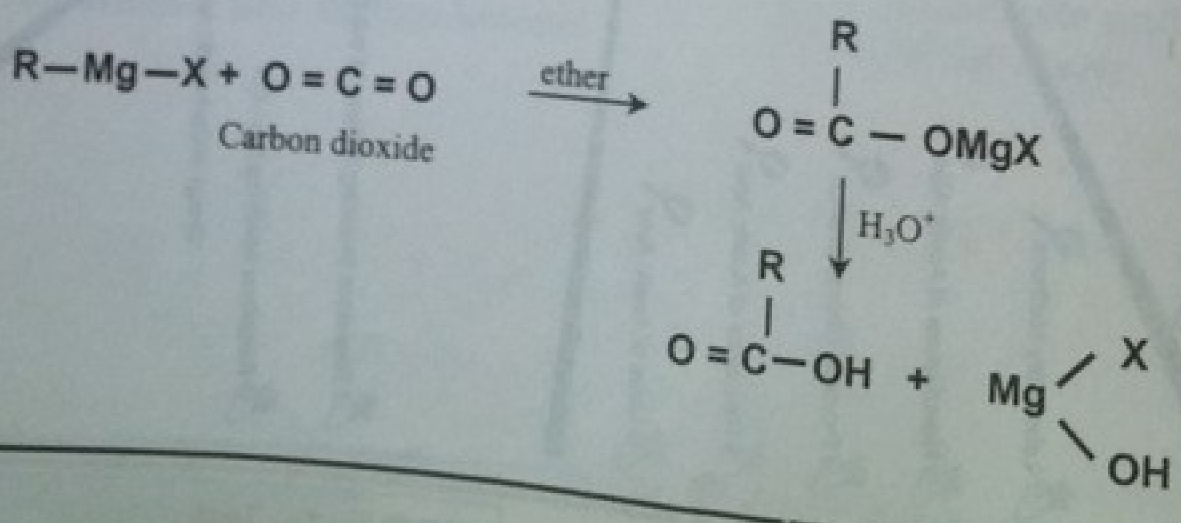
1. From primary alcohols and aldehydes

$$R-CH_2-OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} 2R-CHO \xrightarrow{[O]} R-COOH$$

2. From alkyl nitrile

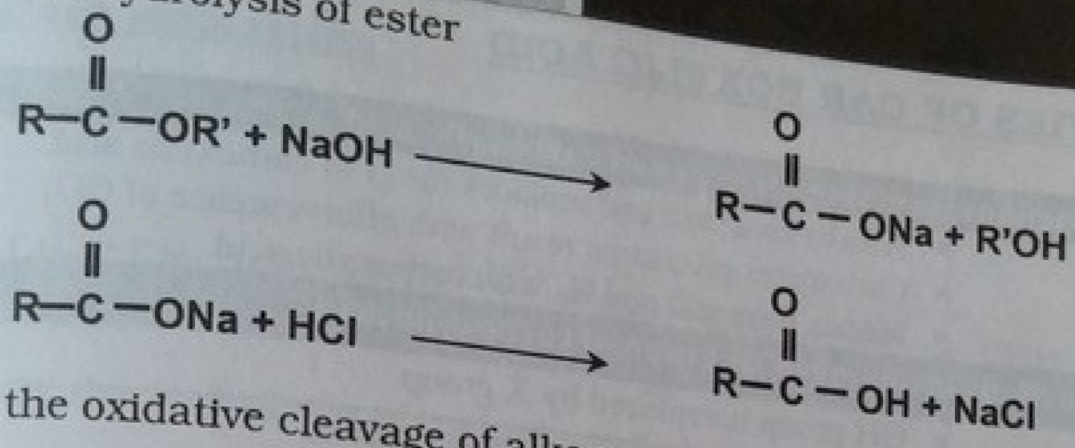
$$R-C\equiv N + H_2O \xrightarrow{H^+ \text{ or } OH^-} R-COOH + NH_3$$

3. From Grignard reagent



$$\underset{}{R-Mg-X} + \underset{\text{Carbon dioxide}}{O=C=O} \xrightarrow{\text{ether}} O=\overset{\overset{R}{|}}{C}-OMgX \xrightarrow{H_3O^+} O=\overset{\overset{R}{|}}{C}-OH + Mg\begin{matrix} / X \\ \backslash OH \end{matrix}$$

4. By the hydrolysis of ester



$$R-\overset{\overset{O}{\|}}{C}-OR' + NaOH \longrightarrow R-\overset{\overset{O}{\|}}{C}-ONa + R'OH$$

$$R-\overset{\overset{O}{\|}}{C}-ONa + HCl \longrightarrow R-\overset{\overset{O}{\|}}{C}-OH + NaCl$$

5. By the oxidative cleavage of alkenes

$$R-CH=CH-R + 4[O] \xrightarrow[\Delta]{KMnO_4, OH^-} 2R-COOH$$

PHYSICIAL PROPERTIES

Smell

C_1 to C_4 have pungent smell and C_4 to C_6 have unpleasant smell.

Solubility

C_1 to C_4 are very soluble in water due to hydrogen bonding. The solubility in water decreases with the increase in molecular mass.

Acetic acid has a cyclic dimmer structure due to intermolecular hydrogen bonding in non polar solvents like benzene.

Boiling Point

The boiling points of carboxylic acids are relatively high due to intermolecular hydrogen bonding.

$HCOOH$	<	CH_3COOH	<	C_2H_5COOH
373K (100°C)		391K(118°C)		424K(141°C)

Melting Point

The melting points of carboxylic acids increase irregularly with molecular mass. Th melting points of carboxylic acids containing even number of carbon atom are highe than the next lower and higher odd members.

CH_3CH_2COOH,	<	$CH_3CH_2CH_2COOH$	>	$CH_3CH_2CH_2CH_2COOH$
251K (-22°C)		267K (-6°C)		237K (-36°C)

REACTIVITY OF CARBOXYL GROUP

- Carbonyl group is electron withdrawing it increases the polarity of -OH.
- The –OH group of carboxylic acid is more active in chemical reactions than those of alcohols.

Types of reaction

- Reaction in which H of carboxylic acid is replaced.
- Reaction in which –OH of carboxylic acid is replaced.
- Reaction involving carboxylic group as whole

CHEMICAL PROPERTIES OF CAR BOXYLIC ACID

Reactions involving –H group of carboxylic acid	
Salt formation	▪ Alkalis form salt and replaces the H of carboxylic acid ▪ Carbonates give same result with effervescence of CO_2 ▪ Metals form salt and H_2 with carboxylic acid
Reactions involving –OH group of carboxylic acid	
Formation of acid halide	▪ OH group is replaced by X group
Ester formation	▪ OH group is replaced by alkoxy radical ▪ Reaction is reversible ▪ Reaction is acid catalyzed
Formation of amide	▪ With NH_3 form ammonium salt on dehydration yield acid amide. ▪ Amides are very stable compound
Formation of acid anhydride	▪ P_2O_5 works as dehydrating agent
Reactions involving carboxyl group	
Partial Reduction of carboxylic acid to alcohol	▪ Reduction of carboxylic group is very difficult ▪ Strong reducing agent like $LiAlH_4$ is used ▪ Reducing agents which are used in aldehydes or ketones cannot be used
Complete Reduction of carboxylic acid to alkanes	▪ Reduction is carried out in the presence of red phosphorus and HI forms alkane

ACETIC ACID

- Its dilute solution is called vinegar. (6 – 10 %)
- In combined form it is present in the form of ester.
- It was first of all derived from vinegar.
- In free form it occurs in a number of fruit juices, which have undergone fermentation.

Ester	Flavour
Amylacetate	Banana
Isobutyl formate	Raspberry
Benzylacetate	Jasmine
Ethyl butyrate	Pineapple
Amyl butyrate	Apricot
Octyl acetate	Orange

PREPARATION OF ACETIC ACID

Laboratory scale	
Oxidation of C_2H_5OH	▪ Dilute H_2SO_4 is used. ▪ First acetaldehyde is formed which then convert into acetic acid
Hydrolysis of CH_3CN	▪ Dilute HCl is used ▪ Acetamide is formed, which on hydrolysis gives CH_3COOH
Industrial scale	
From acetylene	▪ Best source to prepare CH_3COOH ▪ Acetylene is bubbled in 20% H_2SO_4 at 80°C and 1% $HgSO_4$ acting as catalyst results in acetaldehyde ▪ Acetaldehyde changes into acetic acid on oxidation by using V_2O_5 as catalyst ▪ 97% pure acid is obtained
Oxidation of ethanol	▪ 12 % Ethanol is obtained by fermentation of molasses ▪ Oxidation is done by $K_2Cr_2O_7$ and H_2SO_4

Laboratory preparation

(1) By the oxidation of ethyl alcohol or acetaldehyde

$$CH_3-CH_2-OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-CHO \xrightarrow{[O]} CH_3-COOH$$

(2) By the hydrolysis of methyl nitrile

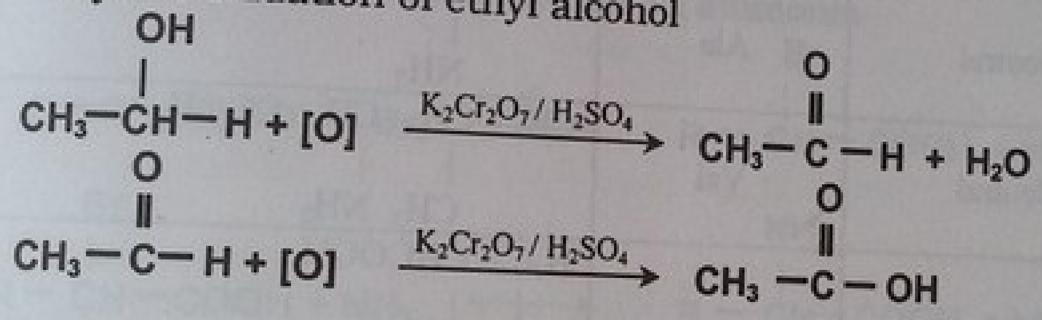
$$CH_3-CN \xrightarrow[H_2O]{\text{dil. HCl}} CH_3-CO-NH_2 \xrightarrow{H_2O/H^+} CH_3-COOH + NH_4^+$$

Industrial preparation

(1) Acetylene

$$HC\equiv CH \xrightarrow[1\%HgSO_4]{20\%\ H_2SO_4} CH_2=CH-OH \xrightarrow[\Delta]{V_2O_5} CH_3-COOH$$

(2) By the oxidation of ethyl alcohol



$$CH_3-\overset{\overset{\large OH}{|}}{C}H-H + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3-\overset{\overset{\large O}{\|}}{C}-H + H_2O$$

$$CH_3-\overset{\overset{\large O}{\|}}{C}-H + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3-\overset{\overset{\large O}{\|}}{C}-OH$$

PHYSICAL CHARACTERISTICS

Properties	Description
Colour, taste and odour	Colourless, sour taste, strong vinegar odour
Melting point, solidifying temperature	16.5°C is M.P, below 16.5°C it solidify (called glacial acetic acid)
Boiling point	118°C
Specific gravity	1.0 gm/cm^3
Solubility	Soluble in ether and alcohol
Existence	Dimer
Uses	**Description**
Chemical industry	Dye stuffs, perfumes, rayon, rubber, copper acetate used in paint
Food industry	Ingredients of food pickles etc
Medical sciences	Preparation of lead acetate for fracture and burns & aluminum acetate used as antiseptic

AMINO ACIDS

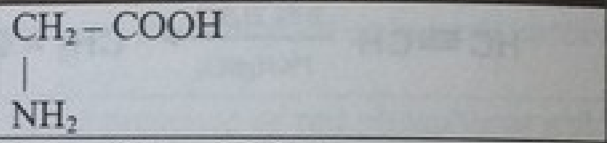
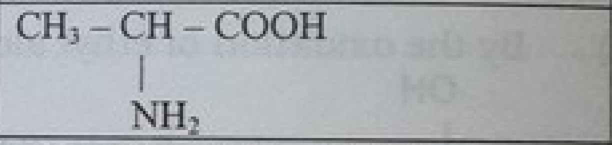
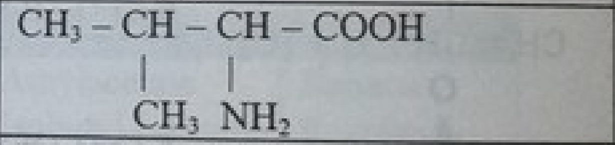
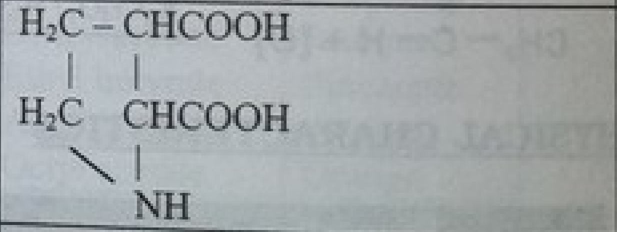
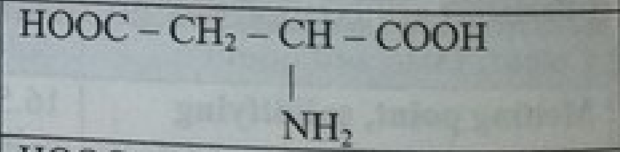
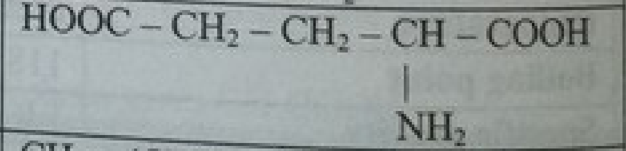
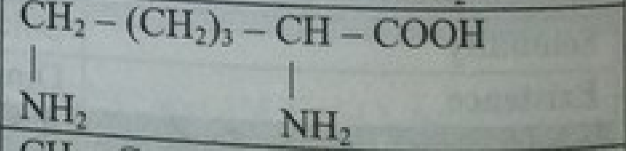
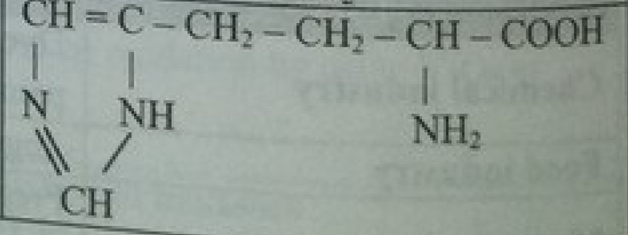
The compounds containing both amino group and carboxylic group are called amino acids.

- α-carbon ⇒ to which carboxyl group is attached
  β-carbon ⇒ to which α-carbon is attached
  γ-carbon ⇒ to which β-carbon is attached.
- Those that cannot be synthesized in our body are called essential amino acid.
- Those that can be synthesized in our body are called non-essential amino acid.

TYPES OF AMINO ACID

On basis of position of amino group

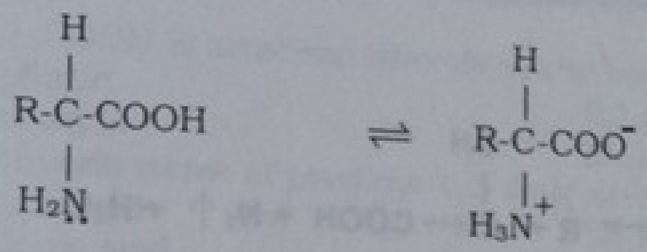
α-amino acid	β-amino acid	γ- amino acid
Amino group is attached to α-carbon e.g. Glycine, analine	Amino acid group is attached to β-carbon e.g. 3-aminopropionic acid, 3-aminobutyric acid	Amino acid is attached to γ-carbon e.g.4-aminobutyric acid

Name	Nature	Abbreviation	Structural formula
1. Glycine	Neutral	Gly	 $\mathrm{\underset{\underset{NH_2}{\mid}}{CH_2}-COOH}$
2. Alanine	Neutral	Ala	 $\mathrm{CH_3-\underset{\underset{NH_2}{\mid}}{CH}-COOH}$
3. Valine	Neutral	Val	 $\mathrm{CH_3-\underset{\underset{CH_3}{\mid}}{CH}-\underset{\underset{NH_2}{\mid}}{CH}-COOH}$
4. Proline	Neutral	Pro	
5. Aspartic acid	Acidic	Asp	 $\mathrm{HOOC-CH_2-\underset{\underset{NH_2}{\mid}}{CH}-COOH}$
6. Glutamic acid	Acidic	Gla	 $\mathrm{HOOC-CH_2-CH_2-\underset{\underset{NH_2}{\mid}}{CH}-COOH}$
7. Lysine	Basic	Lys	 $\mathrm{\underset{\underset{NH_2}{\mid}}{CH_2}-(CH_2)_3-\underset{\underset{NH_2}{\mid}}{CH}-COOH}$
8. Histidine	Basic	His	

ZWITTER ION

The ions which contain positive and negative charge on same molecule is called Zwitter ions.

- Amino acids give zwitter ions.
- On addition of H⁺, -COO part of amino acid accepts H⁺ so acts as base
- On addition of OH⁻, $-NH_3^+$ part liberates H⁺ so acts as acid.



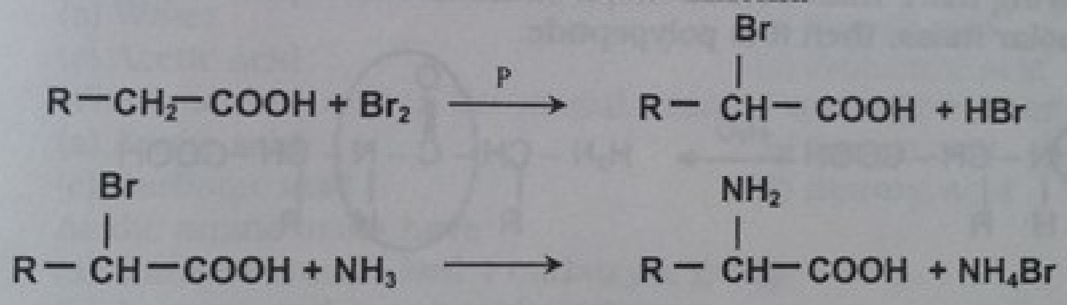
$$R\text{-}\underset{\underset{H_2N}{|}}{\overset{\overset{H}{|}}{C}}\text{-}COOH \rightleftharpoons R\text{-}\underset{\underset{H_3\overset{+}{N}}{|}}{\overset{\overset{H}{|}}{C}}\text{-}COO^-$$

NEUTRAL, ACIDIC, BASIC AMINO ACID

- Amino acid having equal number of amino and carboxylic groups are neutral e.g. glycine.
- Amino acid having more amino group than carboxylic group are basic e.g. Lysine, Arginine, histidine ....
- Amino acid having more carboxylic group than amino group are acidic e.g. aspartic acid, glutamic acid.

SYNTHESIS OF AMINO ACIDS

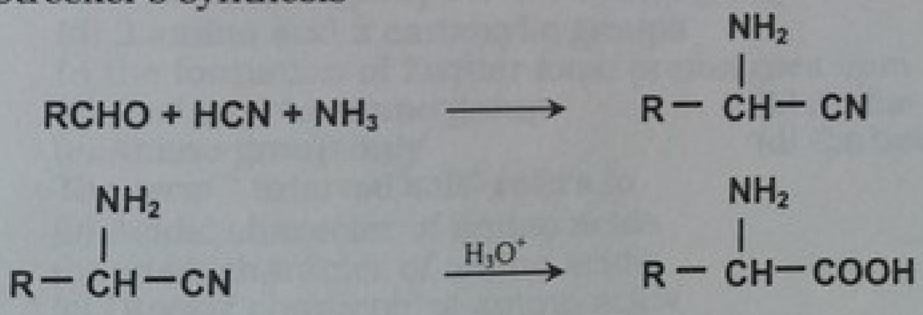
(1) By the reaction of α- bromo acid with ammonia



$$R-CH_2-COOH + Br_2 \xrightarrow{P} R-\underset{}{\overset{\overset{Br}{|}}{CH}}-COOH + HBr$$

$$R-\overset{\overset{Br}{|}}{CH}-COOH + NH_3 \longrightarrow R-\overset{\overset{NH_2}{|}}{CH}-COOH + NH_4Br$$

(2) Strecker's synthesis



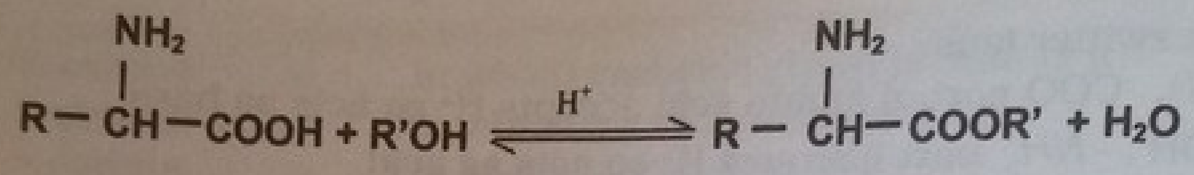
$$RCHO + HCN + NH_3 \longrightarrow R-\overset{\overset{NH_2}{|}}{CH}-CN$$

$$R-\overset{\overset{NH_2}{|}}{CH}-CN \xrightarrow{H_3O^+} R-\overset{\overset{NH_2}{|}}{CH}-COOH$$

REACTIONS OF AMINO ACIDS

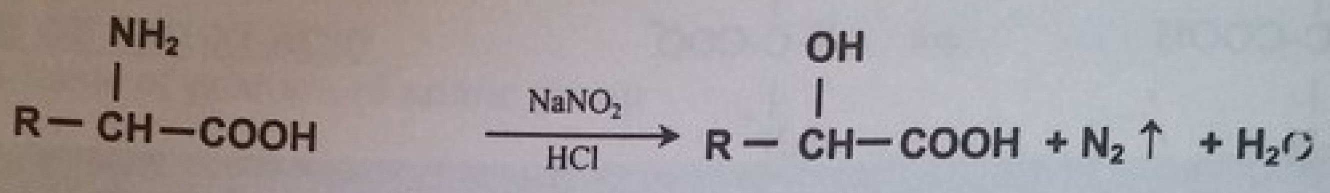
Particulars	Remarks
Esterification	▪Carboxy group reacts with alcohol in the presence of the strong acid forms aminoester.
With nitrous acid	▪Amino group reacts with nitrous acid forming nitrogen gas water and α -hydroxy carboxylic acid.
Ninhydrin Test (DETECTION)	▪ Every amino acid gives bluish violet product.

(1) Esterification



$$R-\overset{\overset{NH_2}{|}}{CH}-COOH + R'OH \overset{H^+}{\rightleftharpoons} R-\overset{\overset{NH_2}{|}}{CH}-COOR' + H_2O$$

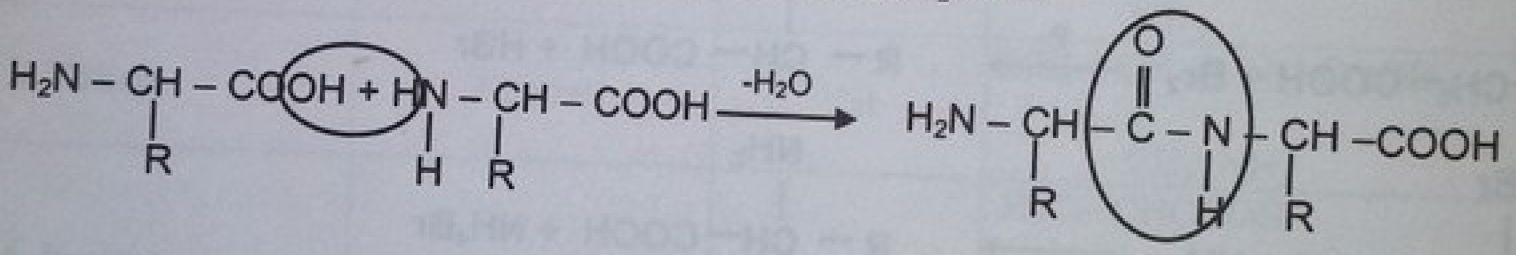
(2) Reaction with Nitrous acid



$$R-\overset{\overset{NH_2}{|}}{CH}-COOH \xrightarrow[HCl]{NaNO_2} R-\overset{\overset{OH}{|}}{CH}-COOH + N_2\uparrow + H_2O$$

PROTEINS AND PEPTIDES

- Peptides are produced, by condensation of amino acids.
- The carboxyl group of one amino acid and amino group of another amino acid gets condensed with elimination of water. The resulting – CO – NH – linkage is called a **peptide linkage.**
- Peptide bond depends upon the number of amino acids per molecule therefore there are dipeptides, tripeptides, polypeptide......etc
- When a large number of amino acids are joined by peptide bonds in a chain, then it is called polypeptide chain.
- Polypeptide having more than 10,000 molar mass is called protein, while if less than 10,000 molar mass, then it is polypeptide.



$$H_2N-\underset{\underset{R}{|}}{CH}-C\boxed{OH + H}\underset{\underset{H}{|}}{N}-\underset{\underset{R}{|}}{CH}-COOH \xrightarrow{-H_2O} H_2N-\underset{\underset{R}{|}}{CH}-\boxed{\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}}-\underset{\underset{R}{|}}{CH}-COOH$$

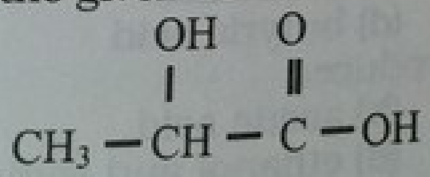
Chapter 13

Carboxylic Acids

PRACTICE EXERCISE

25 mins
Time Yourself

1. When – COOH is attached directly to the benzene ring, the acid is called
   (a) Aliphatic (b) Alicyclic
   (c) Carboxylic (d) Aromatic
2. The common name of propane 1,3-dioic acid is
   (a) Oxalic acid (b) Aromatic acid
   (c) Malonic acid (d) Fumaric acid
3. The common thing in phthalic acid and oxalic acid is that both are
   (a) Aromatic (b) Dicarboxylic
   (c) Hydrocarbons (d) Strong acids
4. The irritation caused by red ant's bite is due to
   (a) Lactic acid (b) Formic acid
   (c) Uric acid (d) Acetic acid
5. The acid which is used as ink remover is
   (a) Oxalic acid (b) Succinic acid
   (c) Adipic acid (d) Acetic acid
6. Which of the following is the strongest acid?
   (a) Water (b) Formic acid
   (c) Acetic acid (d) Propanoic acid
7. Which acid is used in the manufacture of synthetic rubber?
   (a) Acetic acid (b) Formic acid
   (c) Carbonic acid (d) Benzoic acid
8. Acidic amino acids have
   (a) 2 amino groups and 1 carboxylic group
   (b) 1 amino and 1 carboxylic groups
   (c) 2 carboxylic groups and 1 amino group
   (d) 2 amino and 2 carboxylic groups
9. In the formation of Zwitter ions, proton goes from
   (a) Carboxyl to amino group (b) Amino to carboxyl group
   (c) Amino group only (d) Carboxyl group only
10. The term " internal salt" refers to
    (a) Acidic character of amino acids
    (b) Basic character of amino acids
    (c) Dipolar character of amino acids
    (d) Non-polar structure of amino acids
11. The organic acid that does not has COOH group is
    (a) phthalic acid (b) carbolic acid
    (c) Maleic acid (d) Succinic acid
12. The name of the given structure is



$$CH_3-\underset{}{\overset{\overset{\displaystyle OH}{|}}{CH}}-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

    (a) Maleic acid (b) Malonic acid
    (c) Lactic acid (d) Propanol

13. Which one of the following acids is present in lemon juice?
(a) Citric acid
(b) Benzoic acid
(c) Tartaric acid
(d) Oxalic acid

14. The test which is used for the identification of amino acids is
(a) Ninhydrin test
(b) Molisch test
(c) Biuretic test
(d) Benedict test

15. Which one of following amino acid is neither acidic nor a basic in nature?
(a) Lysine
(b) Histidine
(c) Proline
(d) Glutamic acid

16. Carboxylic acid reacts with ammonia to form ammonium salts which on heating produces
(a) CO_2
(b) Alkane
(c) Ester
(d) Acidamide

17. Glycine is the name of an amino acid because
(a) Sweet taste
(b) Bitter taste
(c) Shining appearance
(d) Green colour

18. The complete reduction carboxylic acid results in the formation of
(a) Alkyne
(b) Alkene
(c) Alkane
(d) Alcohol

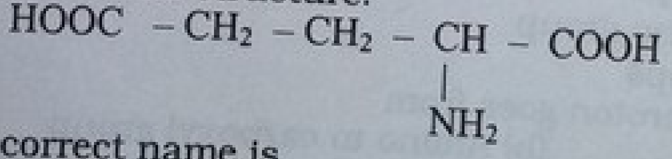
19. The organic acid that can be made from ethanol is
(a) Acetic acid
(b) Formic acid
(c) Butanoic acid
(d) Citric acid

20. Picric acid is
(a) monocarboxylc acid
(b) dicarboxylic acid
(c) aromatic carboxylic acid
(d) none of these

21. The formula of palmitic acid
(a) $C_{15}H_{31}COOH$
(b) $C_{13}H_{27}COOH$
(c) $C_{17}H_{33}COOH$
(d) $C_{17}H_{35}COOH$

22. Essential amino acids are
(a) 5
(b) 10
(c) 15
(d) 20

23. Consider the structure.



$$HOOC-CH_2-CH_2-\underset{\displaystyle NH_2}{\underset{|}{CH}}-COOH$$

Its correct name is
(a) Aspartic acid
(b) Glutamic acid
(c) Palmitic acid
(d) Lactic acid

24. The aliphatic monocarboxylic acids are obtained by the hydrolysis of
(a) proteins and oils
(b) fats and proteins
(c) fats and oils
(d) all above

25. Which of the following is not a fatty acid?
(a) Propanoic acid
(b) Acetic acid
(c) Phthalic acid
(d) Butanoic acid

26. An acid with unpleasant smell
(a) formic acid
(b) acetic acid
(c) propionic acid
(d) butyric acid

27. The basic hydrolysis of ethyl acetate produces
(a) ethanol
(b) acetic acid
(c) ethanol and acetic acid
(d) ethanol and sodium acetate

28. Carboxylic acid on reduction with HI / phosphorous yields
(a) alkane
(b) alcohols
(c) aldehydes
(d) ketones

29. Which of the following is not an ester
(a) amyl acetate
(b) sodium butyrate
(c) isobutyle formate
(d) octyl acetate

30. The reaction of carboxylic acids with alcohols in presence of cone. H_2SO_4 is called
(a) esterification
(b) neutralization
(c) hydrolysis
(d) saponification

31. Which of the following has orange flavour
(a) isobutyl formate
(b) octyl acetate
(c) ethyl butyrate
(d) amyl lactate

32. Which of the following is not an amino acids
(a) glumatic acid
(b) lactic acid
(c) aspartic acids
(d) glycine

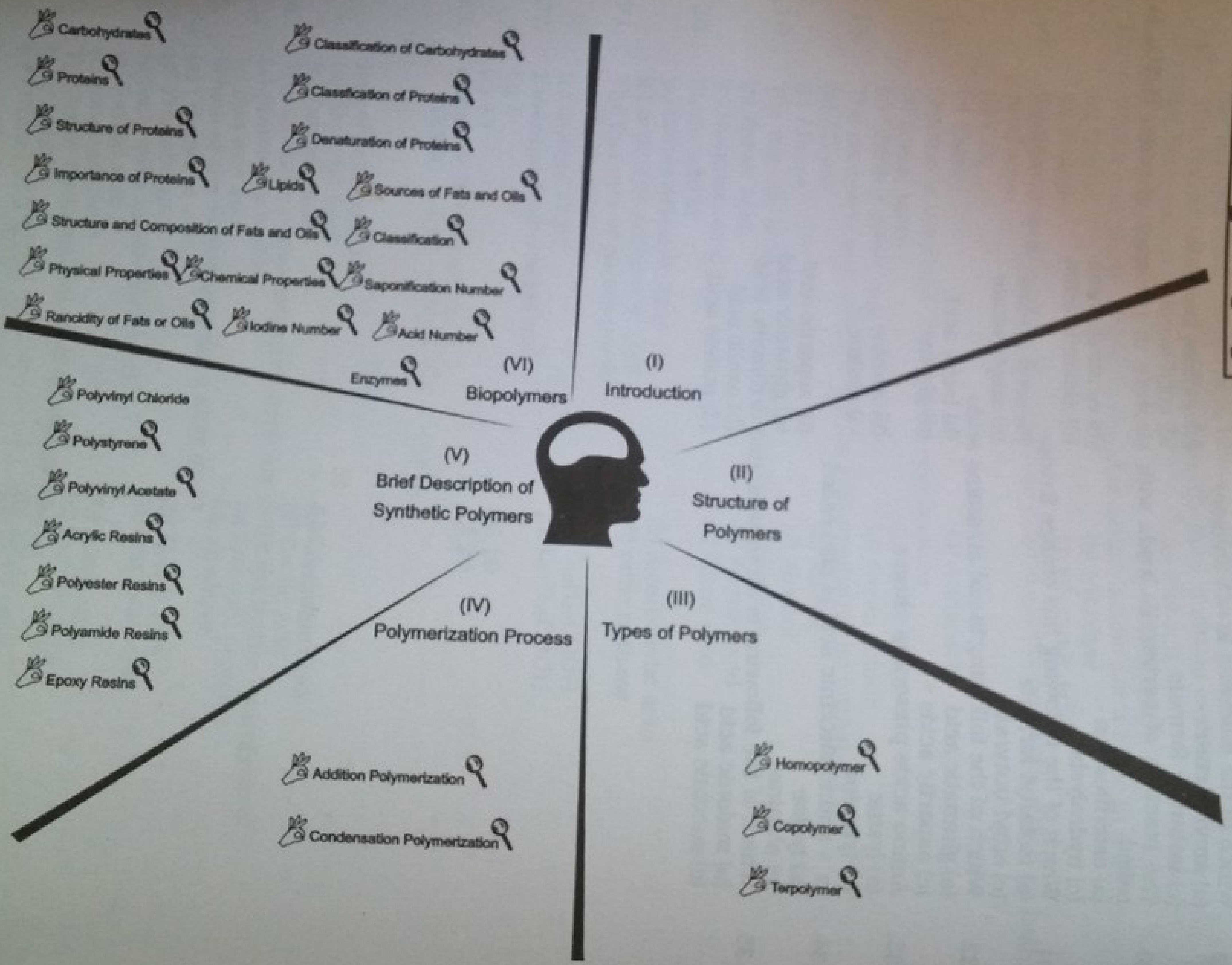
33. Amino acids present in cheese
(a) lysine
(b) alanine
(c) tyrosine
(d) proline

34. α - amino succinic acid is also called
(a) lysine
(b) aspartic acid
(c) alanine
(d) glutamic acid

35. Which of the following is an unsaturated carboxylic acid
(a) malonic acid
(b) oxalic acid
(c) succinic acid
(d) maleic acid

Chapter 14

MACROMOLECULES



Chapter 14

Macromolecules

MACROMOLECULE

A giant molecule which is often a polymer is called macromolecule.

POLYMER

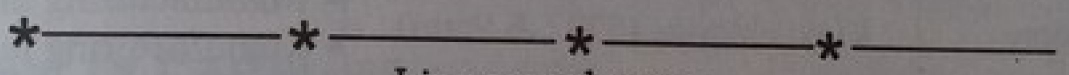
A large molecule build up by the repetition of small and simple chemical units is called polymer.

MONOMER

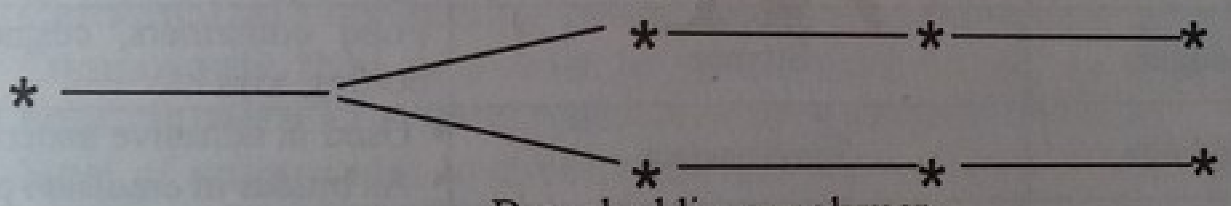
Small units or simple molecule from which macromolecules are formed are called monomers.

STRUCTURE OF POLYMERS

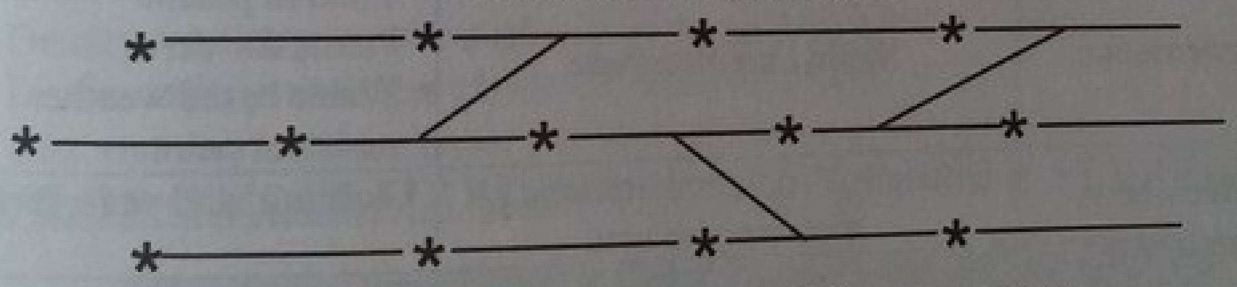
Particular	Description
Linear polymer	Monomers are arranged in line.
Branched linear polymer	Monomers are arranged in line and are branched.
Interconnected polymer	Chains of polymers linked through branches.
Degree of polymerization	Number of repeating unit in polymer is called degree of polymerization. (DP)
Molecular mass of polymer	Molecular mass of repeat unit × DP



Linear polymer



Branched linear polymer



Cross-linked linear polymer or Interconnected

TYPES OF POLYMERS ON THE BASIS OF MONOMER

Particular	Homopolymer	Copolymer	Terpolymer
Composition	Single type of polymer.	Two types of monomer	Three types of monomer
Example	Vinyl acetate	Vinyl acetate and butyl maleate	Butyl acrylate, methacrylate and acrylic acid

Thermoplastic polymers	Thermosetting polymers
The polymers that can softened repeatedly when heated and hardened when cooled.	The polymers that become hard on heating and cannot softened again.

Chapter 14 Macromolecules

POLYMERIZATION

In 1929, W.H Carothers suggested a classification of the polymerization process into two types depending upon the way the polymers are formed.

i. Addition polymerization
ii. Condensation polymerization

Addition polymerization	Condensation polymerization
Empirical formula of monomer and polymer is same	Empirical formula of polymer and monomer is different
No by-product are produced.	By-product are produced
Reaction takes place in main chain through free radical mechanism	Reaction takes place through functional groups
Example: Polyethylene, PVC…	Example: Bakelite Nylon….

IMPORTANT SYNTHETIC POLYMER

Name of polymer	Polymerization Type	Monomers present	Uses
Polyvinyl chloride	Addition	Vinyl chloride (52°C & 9atm)	▪ Used in floor covering ▪ Manufacturing in pipe ▪ Manufacturing in gramophone recorders
Polystyrene	Addition	Styrene	Food containers, cosmetics, bottles, toys etc.
Polyvinyl acetate	Addition	Vinyl acetate	▪ Used in adhesive material ▪ As binder in emulsion paint
Acrylic resins	Condensation	Methyl methacrylate	▪ Used in plastic ▪ Paints for cars ▪ Water based weather resistant paint
Polyester resins	Condensation	Ethane 1,2 - diol and benzene1,4 - dicarboxylic acid	Clothing and water tanks.
Polyamide resin	Condensation	Diamines(hexame thylenediamine) and aliphatic dicarboxylic acid (adipic acid)	Textile fibre
Epoxy resins	Condensation	2,2-Diphenylol propane and epichloro hydrin	Used as coating material adhesion and chemical resistant

Chapter 14

Macromolecules

BIOPOLYMERS

CARBOHYDRATES

The compounds containing polyhydroxy, ketone or aldehyde, which on hydrolysis give polyhydroxy aldehyde or ketone or their derivatives are called carbohydrates.

CLASSIFICATION OF CARBOHYDRATES

Particular	Monosaccharide	Oligosaccharide	Polysaccharide
Definition	Cannot hydrolyze	Can hydrolyze and give two to nine monosaccharide units	Can hydrolyze and give numerous monosaccharide units
Solubility	Soluble in water	Less soluble	Not soluble
Taste	Sweet	Sweet	Tasteless
Branches	Absent	Absent	Present
Structure	Crystalline solid	Crystalline solid	Amorphous solid

NAMING OF MONOSACCHARIDE DEPENDING UPON NUMBER OF C ATOMS

No. of C atom	Name	Example
03	Triose	Glyceraldehyde
04	Tetraose	Erythrose
05	Pentose	Ribose
06	Hexose	Glucose

ISOMERISM IN CARBOHYDRATES

- Carbohydrate containing aldehyde is called aldose and ketone is called ketose.
- Compounds that can exist in open chain as well as in cyclic structure called **enantiomers**.Enantiomerism is present in carbohydrates.
- Most of sugar exist in cyclic structure (pentagonal or hexagonal).
- Carbohydrates are optical active compounds.
- Dextrorotatory rotates plane of polarized light to right.
- Levorotatory rotates plane of polarized light to left.
- Glucose is dextrorotatory while fructose is levorotatory.

NAMING OF OLIGOSACCHARIDE DEPENDS UPON NUMBER OF C ATOMS

Monosaccharide units	Name	Example
02 units	Disaccharide	Lactose
03 units	Trisaccharide	Raffinose

IMPORTANT POLYSACCHARIDES

Particular	Starch	Glycogen	Cellulose
Occurrence	Plant (stored food of plant)	Animal (stored food)	Plant(cell wall)
Monomer	Glucose-D	Glucose-D	Glucose-D
Glycosidic linkage	α-1,4 and α-1,6	α-1,4 and α-1,6	β-1,4
Structure	Amylose and amylopectin	Like amylopectin	Linear chain
Action of enzyme	Digested by amylase	Digested by amylase	Digested by cellulase but not present in human

Chapter 14

Macromolecules

PROTEINS

- The name protein is derived from the Greek word PROTEIOS meaning of prime importance.
- Proteins are polymer of amino acids.
- Proteins may be defined as the high molecular weight organic materials, which upon complete hydrolysis, yield amino acids.

TYPES OF PROTEINS

Particular	Simple protein	Conjugated protein	Derived protein
Definition	Gives only amino acid and its derivatives	Gives amino acid and prosthetic group	Contains amino acids and substances derived from conjugated protein
Examples	Globulins, albumins, collagens	Lipoproteins, phosphoproteins	Peptones, oligopeptides, enzyme, proteoses, polypeptides

STRUCTURE OF PROTEINS

- The bond in which amino group and carboxylic group reacts and form bond with elimination of water molecule is called peptide bond.
- Protein molecule contains large number of peptide bonds called polypeptide bonds.

Three different structures of proteins

1) Primary structure (sequence of amino acid in peptide chain)
2) Secondary structure (regular coiling or zigzagging of polypeptide chain caused by hydrogen bonding.
3) Tertiary structure (three dimensional twisting and folding of polypeptide chain)

DENATURATION OF PROTEINS

Denaturation of proteins can be done by:

a) Heat: albumin of egg white changes into solid
b) Change in pH: each enzyme has its own particular pH for action
c) Oxidizing or reducing conditions

IMPORTANCE OF PROTEINS

Field	Usage
Organisms	Protoplasm contains proteins
Inheritance	Nucleoplasm contains nucleoproteins which controls the characters in next generation
Enzymes	All are biocatalytical proteins
Special function	Proteins have special function as haemoglobin which is a protein present in blood, insulin and thyroxin etc.
Industry	In preparation of leather, tanning of hide produced by reactions of tannic acid with protein, gelatin, caesein,....

LIPIDS

- Derived from Greek word 'lipos' means fats
- Natural occurring organic compounds present in animal and plant
- Soluble in organic solvent
- Insoluble in water
- Derived from fatty acid, glycerol and steroids

SOURCES OF FATS AND OILS

Source	Lipids obtained
Animal	▪ Fat is present in adipose tissue ▪ Butter and ghee derived from milk
Plant	▪ Oils are present in seeds and nuts ▪ Soya been oil, cotton seed oil
Marine	▪ Oil obtained from salmons etc.

STRUCTURE AND COMPOSITION OF FATS

Oils	Fats
Triglyceride of higher fatty acids	Triglyceride of higher fatty acids
Liquid in nature	Solid in nature usually
Degree of unsaturation is high	Degree of saturation is high
Low melting points	Higher melting points than oils
Gives addition reactions with hydrogen gas	No addition reaction
High Iodine number	Low Iodine number

NOTE:

Animal fats or oils are esters of glycerol and fatty acids called triglycerides.

CLASSIFICATION OF LIPIDS

- Simple lipids: ester of fatty acid with glycerol.
- Compound lipids: contains radicals in addition to fatty acids, alcohol, glycerol, phospholipid, sphingolipid & lipoproteins.
- Derived or associated proteins: hydrolytic products of lipids are called associated lipids. e.g. sterols, vitamin D and terpenes.

PROPERTIES

Particular	Remarks
Hydrolysis	▪ Addition of water by breakage of O-H bond ▪ Lipids gives fatty acid and glycerol
Saponification	▪ Hydrolysis of fat or an oil with an alkali is called saponification. ▪ This reaction is also used in making of soap and candles.
Hardening of oils	▪ Hydrogenation is conducted in presence of catalyst. ▪ Unsaturated oil changes into saturated semi-solid fats. ▪ This reaction is used in ghee industry.
Appearance	Non-crystalline solid at room temperature
Odour, colour and taste	Odourless, colourless, tasteless
Solubility	Insoluble in water but soluble in organic solvent
Conductance	Poor conductor of heat and electricity.

SAPONIFICATION NUMBER

It is the number of milligram of KOH required to saponify one gram of fat or oil.

- One gram of glycerol tripalmitate require 168000mg of KOH.
- Saponification number of glycerol palmitate is 208.

RANCIDITY OF FATS OR OILS

Bad odour that comes from oil or fat spoilage is called rancidity.

- It is due to hydrolytic or oxidative reactions, which releases foul smell of aldehydes and fatty acids.
- Oil from sea animal deteriorates rapidly.

IODINE NUMBER

It is the grams of iodine added to 100g of fat or oil.

- Iodine number determines extent upon degree of unsaturation.
- Glyceride with no double bond has iodine number 200.

ACID NUMBER

It is the milligrams of KOH required to neutralize one gram of fat. It tells amount of the free fatty acid.

STEROIDS

Lipids having "perhydroxycyclopentanophenanthrene" ring in its structure are called steroids.

- Perhydroxycyclopentanophenanthrene contains three hexagonal and one pentagonal ring.

IMPORTANT STEROIDS

Cholesterol	Ergosterol	Phospholipids
Present in animal tissues	Present in fungi and yeast	Present in animals
Found in free state or esterified form in blood	In ultraviolet rays, it changes into vitamin-D.	Two hydroxyl group are esterified with fatty acid while third hydroxyl group of glycerol forms link with phosphoric acid or its derivative
Accumulation of cholesterol cause plaque like deposits in arteries	-	-

ENZYMES

Enzymes are biocatalytical proteins that increases rate of reaction.

- Each enzyme catalyzes only one reaction.
- Enzymes can increase rate of reaction by 10^{20} times.
- The space at which substrate attaches is called active site.
- Proteinaceous part of enzyme called apoenzyme, non-protineous part is called co-enzyme.
- Co-enzyme contains Fe^{+2}, Zn^{+2}, Mg^{+2}

- Some enzymes contain vitamin as co-enzyme e.g nicotinoamide adenine dinucelotide contains nictinoamide vitamin and thiamine pyrophosphotase contains vitamin B_1.
- Suffix "ase" is added to the name of substrate for naming of enzymes.

CLASSIFICATION OF ENZYMES

IUB classified the enzymes in the following six classes

Particular	Description
Oxidoreductase	Catalyze oxidation-reduction reaction e.g. oxidase dehydrogenase and peroxidase etc.
Transferases	Exchange of functional group e.g. phosphotransferase
Hydrolases	Catalyze hydrolysis e.g. proteolytic enzymes
Lyases	Catalyze addition of ammonia water or CO_2 to double bonds e.g. fumarase
Ligases	Links two molecules together e.g. succinic thiokinase, carboxylase etc.
Isomrases	Catalyze transfer of group within molecule e.g. phospho glyceromutases

PROPERTIES OF ENZYMES

Property	Description
Specificity	Each enzyme can catalyze on one reaction. e.g. hexokinase catalyzes the conversion of hexose to their 6-phosphate derivatives
Protein nature	Enzymes are proteinaceous in nature usually.
Direction of enzyme reaction	Enzyme reactions are reversible
Isoenzyme	Two enzymes that are distinct chemically and physically but catalyze same reaction.

FACTORS AFFECTING ENZYME ACTIVITY

Factor	Description
Enzyme concentration	Enzymatic reaction is directly proportional to concentration of substrate and square root of enzyme concentration.
Temperature	▪ 37°C is suitable temperature called optimum temperature. ▪ High temperature destroys enzymes.
Effect of pH	Optimum pH is 6.4 to 6.9 for salivary amylase.
Other substances	▪ Co-enzymes and activator increase activity of enzyme. ▪ Inhibitor retards enzyme activity.
Radiations	Enzymes are inactivated by exposure of ultraviolet rays, beta rays, gamma rays and X-rays.

NUCLEIC ACID

- In pus cell, nucleic acid was discovered in1868 and in 1872, in sperm head, by Fredrick Miescher.
- It is present in nucleus of animals, plants and virus cell.
- Nucleic acid helps in transmission of genetic information and mutation.

TYPES OF NUCLEIC ACID

RNA	DNA
Oxyribose nucleic acid	Deoxyribose nucleic acid
Mostly present in cytoplasm	Present in DNA
Help in protein synthesis	Help in genetic transmission
Molecule contains single strand	Molecule contains double helical structure
Uracil nitrogenous base is present	Thiamine is present
Hydrogen bonding is absent	Hydrogen bonding is present
Ribose sugar is present	Dexoyribose sugar is present
It dos not replicate	It replicates

COMPOSITION OF DNA

Each nucleotide of DNA contains:

- Sugar (pentose sugar)
- Phosphoric acid
- Nitrogen bases
    - Purine bases: adenine, guanine
    - Pyrimidine bases: cytosine, uracil and thiamine

Chapter 14

Macromolecules

PRACTICE EXERCISE

20 mins
Time Yourself

1. Polymers described as large molecules built up from small repeating units called
   - (a) Biopolymers
   - (b) Dimers
   - (c) Monomers
   - (d) metamers
2. A polymer in which three different monomers combine called.
   - (a) Copolymer
   - (b) Terpolymer
   - (c) Homopolymer
   - (d) Biopolymer
3. The important monomers of acryclic resins is
   - (a) Vinyl chloride
   - (b) Styrene
   - (c) Methylmethacrylate
   - (d) Hexamethylenediamine
4. Polyester resins are the product of the reaction of
   - (a) Dihydric alcohol and dicarboxylic aromatic acids
   - (b) Polyamines with aliphatic dicarboxylic acids
   - (c) Styrene in the presence of catalyst
   - (d) Epichlorohydrin with diphenylol propane
5. Industrial materials and thermal power stations are coated with
   - (a) Polyester resins
   - (b) Epoxy paints
   - (c) Polyamide resins
   - (d) Polyvinyl chloride
6. Carbohydrates are polyhydroxy compounds of
   - (a) Glucose
   - (b) Glyceraldehydes
   - (c) Oligosaccharides
   - (d) Aldehydes and ketones
7. Common example of carbohydrates are
   - (a) Cellulose, glycogen, galactose
   - (b) Glyceraldehydes, glucose, peptone
   - (c) Glycerol, phospho-lipids, collagen
   - (d) Legumin, amylopectin, albumin
8. Nylon is obtained by heating
   - (a) Acrylic acid
   - (b) Epichlorohydrin
   - (c) Vinyl chloride
   - (d) Adipic acid with hexamethylene diamine
9. Hydrolysis of an oligosaccharide in the presence of acid yields
   - (a) One monosaccharide unit
   - (b) No monosaccharide unit
   - (c) 2-9 monosaccharide unit
   - (d) many monosaccharide
10. Amylose is
    - (a) Soluble in water
    - (b) Insoluble in water
    - (c) Soluble in alcohol
    - (d) Partially soluble in alcohol
11. The process of polymerization was classified by
    - (a) Strecker
    - (b) Sabatier
    - (c) Runge
    - (d) W. H. Carothers
12. All proteins yield ____________ upon complete hydrolysis.
    - (a) Nitrogen
    - (b) Amino acids
    - (c) Carbon and hydrogen
    - (d) Sulphur

13. Protein attached to some non protein group is called
(a) Derived protein (b) Sample protein
(c) Proteoses (d) Conjugated protein

14. Regular coiling or zigzagging of polypeptide through hydrogen bonding is its.
(a) Quantum structure (b) Secondary structure
(c) Tertiary structure (d) Primary structure

15. Orgosterol is
(a) Orgocalciferol (b) Vitamin D_2
(c) Sterol (d) All of the above

16. Lipids are soluble in
(a) Organic solvents
(b) Organic and inorganic solvents
(c) Inorganic solvents
(d) Solubility has nothing to do with lipids

17. Animal fats are located particularly in
(a) Skeleton tissues (b) Cardiac tissues
(c) Connective tissues (d) Adipose tissues

18. Animal and vegetable fats are
(a) Glycerols
(b) Fatty acids
(c) Triesters formed from glycerol and fatty acids
(d) Tetraesters formed from glycerol and fatty acids

19. Lipopolysaccharides are examples of
(a) Derived lipids (b) Simple lipids
(c) Compound lipids (d) Not a type of lipids

20. Triglycerides are easily hydrolyzed by enzymes called
(a) Lyases (b) Ligases
(c) Lipases (d) Hydrolases

21. Saponification is the hydrolysis of fat or oil with an
(a) Acid (b) Alkali
(c) Enzyme and alkali (d) Enzyme and acid

22. Enzymes that catalyze the transfer of groups within molecule are called
(a) Isomerases (b) Lyases
(c) Transferases (d) Ligases

23. Enzymes from the same organism which catalyze same reaction but are chemically and physically distinct from each other are called
(a) Oxidoreductases (b) Hydrolases
(c) Isoenzymes (d) Isomerases

24. Rate of enzymatic reaction is directly proportional to the concentration of
(a) Enzyme (b) Substrate
(c) Enzyme and substrate (d) Enzyme and product

25. Enzyme proved useful in cancer treatment is
(a) Lactic dehydrogenase (b) Alkaline phosphatase
(c) L-asparaginase (d) Cellulase

26. Purines and pyrimidines are
(a) Enzymes (b) Nitrogenous bases
(c) Carbohydrates (d) Lipids

27. Nucleic acids were first demonstrated in
(a) Pus cells (b) Sperm heads
(c) 1872 (d) All of the above

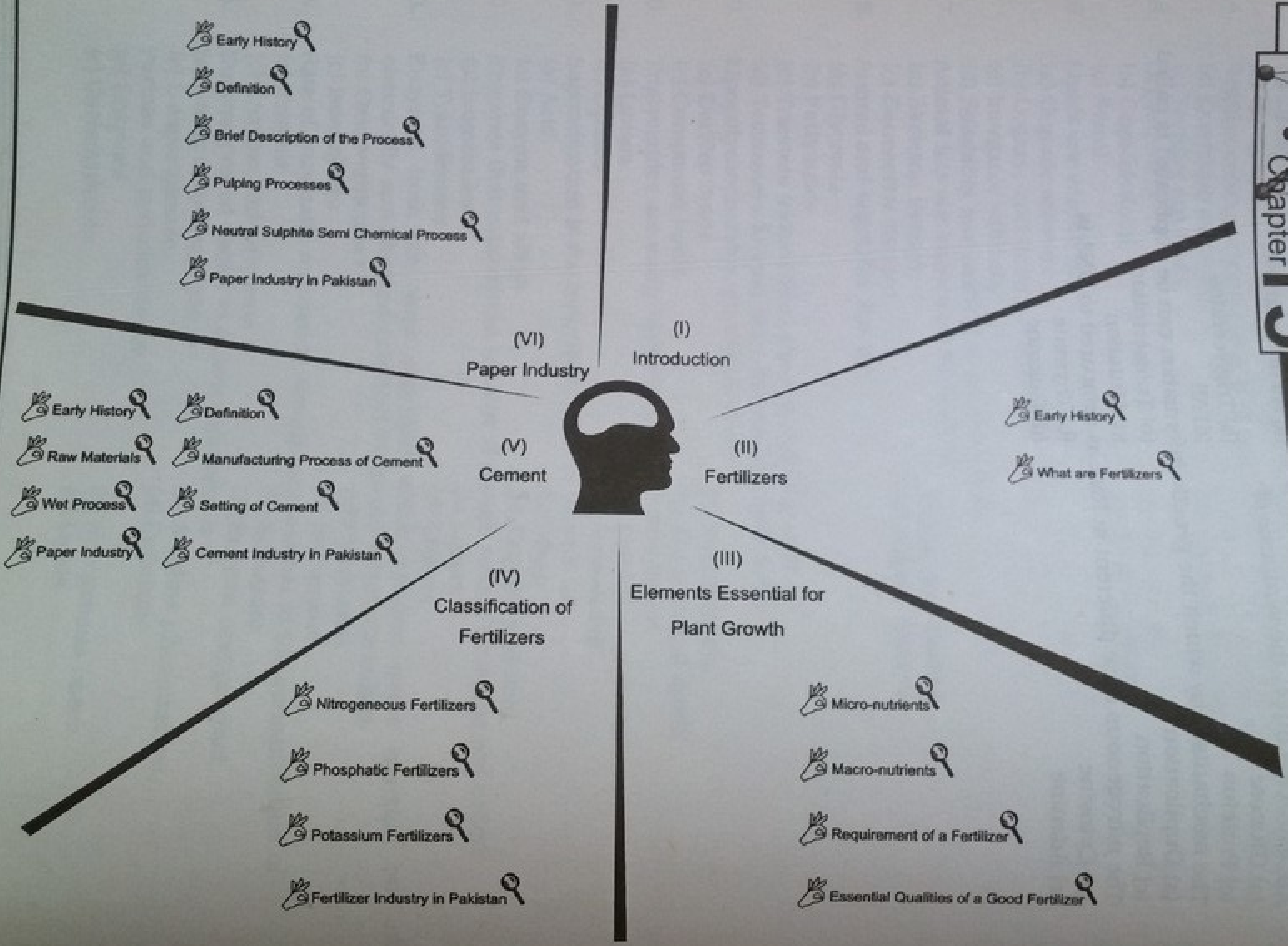
28. Nucleic acids direct the synthesis of
(a) Glucose (b) Triglycerides
(c) Proteins (d) All

29. The mechanism by which the genetic information can be duplicated is called
(a) Duplication (b) Transcription
(c) Replication (d) Mutation

30. The nitrogenous base different in RNA as compared to DNA is
(a) Cytosine (b) Thymine
(c) Adenine (d) Guanine

Chapter 15

COMMON CHEMICAL INDUSTRIES IN PAKISTAN



- (I) Introduction
  - Early History
  - What are Fertilizers
- (II) Fertilizers
- (III) Elements Essential for Plant Growth
  - Micro-nutrients
  - Macro-nutrients
  - Requirement of a Fertilizer
  - Essential Qualities of a Good Fertilizer
- (IV) Classification of Fertilizers
  - Nitrogeneous Fertilizers
  - Phosphatic Fertilizers
  - Potassium Fertilizers
  - Fertilizer Industry in Pakistan
- (V) Cement
  - Early History
  - Raw Materials
  - Wet Process
  - Paper Industry
  - Definition
  - Manufacturing Process of Cement
  - Setting of Cement
  - Cement Industry in Pakistan
- (VI) Paper Industry
  - Early History
  - Definition
  - Brief Description of the Process
  - Pulping Processes
  - Neutral Sulphite Semi Chemical Process
  - Paper Industry in Pakistan

Chapter 15

Common Chemical Industries in Pakistan

ESSENTIAL ELEMENTS FOR PLANT GROWTH

Micronutrients	Macro nutrients
Required in a very small amount	Required in a large amount
Includes B, Cu, Fe, Mn, Zn, Mo, Cl	Includes N, P, K, Ca, Mg, S, C, H, O
Requirement is 6-200gms/acre	Requirement is 5kg to 200kg/acre

FERTILIZER

The compounds that are added to soil to make up deficiency of elements required for growth of plants are called fertilizers.

- Manure is an organic compound obtained from faeces and urine of livestock.
- Manure was used as fertilizer in Chinese society.
- N, P, K are having primary importance for growth of plant.
- S, Mg, Ca are considered as secondary importance for growth of plant.

QUALITIES OF GOOD FERTILIZER

- Readily available to plant
- Soluble in water
- Is not injurious to plant
- Should be cheap
- Should be of high stability
- Do not change the pH of soil
- Easily assimilated by plant

CLASSIFICATION OF FERTILIZERS

Nitrogenous fertilizer	Phosphate fertilizer	Potassium fertilizer
Nitrogen (N) is supplied	Phosphorus (P) is supplied	Potassium (K) is supplied
Increases yield and quality of plant	Increases fruit and seed formation process of plant	Starch, sugar and fibrous material formation enhances
Imparts green colour to leaf	Increases resistance to disease	Increases the resistance and makes root of plant healthy
Ammonia is used in liquid while other fertilizers are used as solids	Diammonium phosphate and calcium super phosphate (solids) are widely used	KNO_3 is commonly used
Except $Ca(NO_3)_2$, $NaNO_3$, these increase the acidity of soil	It fulfils 75% nutrient requirement of plant	It helps in ripening of seed and fruit
Urea contains 46% N.	It contains 16%N, 48%P_2O_5	It contains 13%N, 44%K.
Urea is prepared from CO_2 and liquid ammonia	It is produced by the reaction of ammonia and phosphoric acid	KNO_3 is prepared from $NaNO_3$ and KCl

- 14 fertilizer plants are working in Pakistan
- Production of fertilizer is 56.30.100 million tons/annum

CEMENT

Cement is a material produced by burning an intimate mixture of calcarious (75%) and argillaceous (25%) material.

- Mason Joseph Aspadin introduced cement (Portland cement).

Chapter 15 Common Chemical Industries in Pakistan

COMPOSITION OF GOOD CEMENT

Compound	%age
Lime	62
Silica	22
Alumina	7.5
Magnesia	2.5
Iron oxide	2.5
Sulphur trioxide	1.5
Sodium oxide	1.0
Potassium oxide	1.0

The essential constituents are lime, silica and alumina.

RAW MATERIALS FOR CEMENT

Name	Contents	Function
Calcarious material	Limestone, marble, chalks, marine shells	Source of CaO
Argillaceous material	Clay, shale, slate, blast furnace slag	Provide acidic components
Gypsum	Calcium sulphate hydrate	Strength

MANUFACTURING OF CEMENT

- There are 22 factories of cements in Pakistan
- Production of cement is 9,578,802 million tons/annum
- Two methods are available for manufacturing of cement
    1. Wet process
    2. Dry process

Wet process

Wet process involves five stages.

1. Crushing or Grinding
    - Ball mill is used.
2. Mixing of raw material
    - 75% limestone and 25% clay is mixed and slurry is produced.
    - Slurry contains 35 to 45% water
3. Heating of slurry
    - Heating is conducted in inclined kiln.
    - Rate of revolution of kiln is 1-2 r.p.m
    - The charge takes 2.3hrs in kiln to complete heating process
    - In drying or pre-heating zone of kiln the temperature is 500°C & clay is broken down into Al_2O_3, SiO_2 and Fe_2O_3.
    - In decomposition zone of kiln the temperature remains 800°C & $CaCO_3$ is broken down into CaO and CO_2.
    - In burning zone of kiln the temperature is 1500°C & calcium silicate, calcium aluminate and calcium ferrite are formed
    - the material is cooled down upto 150-200°C in cooling zone
4. Clinker formation
    - Material from kiln is called clinker.
5. Grinding of clinker with gypsum
    - 2% gypsum is added to clinker.

SETTING OF CEMENT

In first 24 hours

- After mixing with water, tri-calcium aluminate is added that absorbs water and form colloidal gel ($3Ca.Al_2O_3.H_2O$)
- Gypsum changes into $Ca.Al_2O_3.3CaSO_4.2H_2O$ (calcium sulpho- aluminate).

Between 1-7 days.

- Tri calcium salts hydrolyze to yield Ca and Al hydroxides.
- $Ca(OH)_2$ and $Al(OH)_3$ are produced.
- $Ca(OH)_2$ has needle- shaped crystals, which gives strength to cement
- $Al(OH)_3$ fills the interstices and hardens the cement.

PAPER INDUSTRY

It is a sheet material made up of network of natural cellulosic fibres, which have been deposited from a suspension (aqueous).

- The consumption of paper in Pakistan is 5kg/man/year

RAW MATERIAL OF PAPER

Non woody material	Woody raw material
• Wheat straws • Corn straws • Rice straws • Bagasse • Rag • Bamboo • Cotton stalk • Kahi • Grasses	• Poplar • Eucalyptus • Fur

PULPING METHODS

There are three principal methods available.

- Kraft process (alkaline)
- Sulphite process (acidic)
- Neutral Sulphite Semi Chemical Process (NSSC)

NSSC

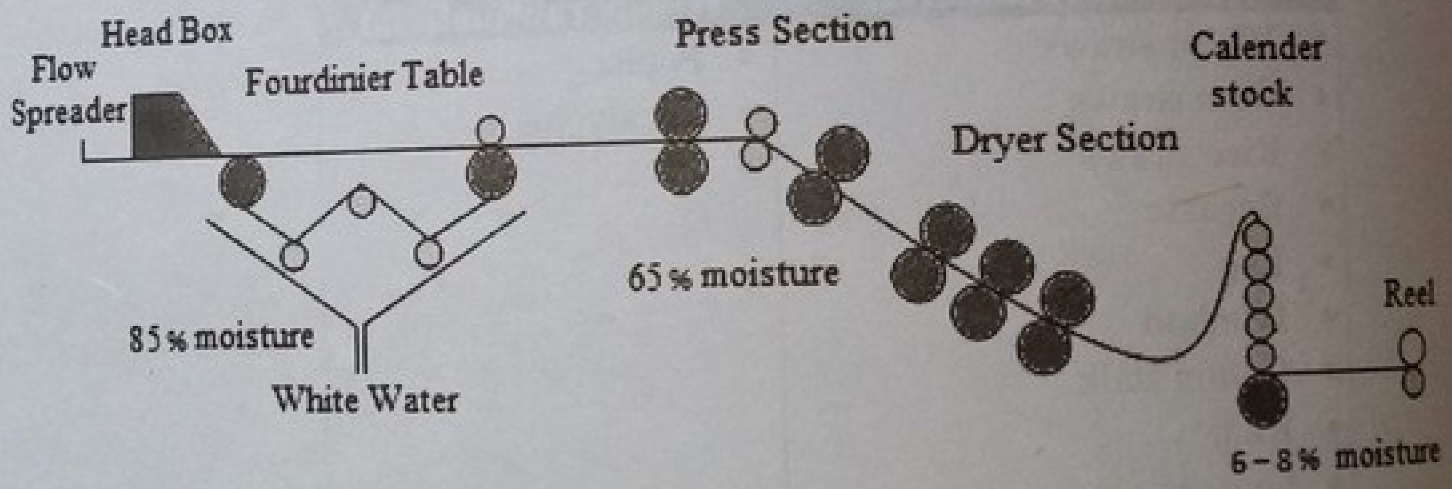
NSSC involves following manufacturing steps

1. Cutting of raw material
2. Dry cleaning
3. Wet cleaning
4. Screening
    - Magnetic separator separates iron piece
    - Stones are separated by centri-cleaners
5. Digester
    - Digester is made up of steel and wrought iron
    - r.p.m of digester is 2.50 and temperature is maintained 160-180°C.
    - PH 7-9 buffered with Na_2CO_3 + NaOH

NSSC is dominant over other due to chemical recovery and pulp strength.

6. Blow tank
   - Separates cooked and uncooked material
7. Pulp washing
   - Cooked material is washed with water by using 80-mesh sieve.
   - Due to presence of lignin, paper becomes brittle.
   - Bleaching of pulp is done by Cl_2 and sodium hypochlorite.
8. Stock preparation plant
   - Dispersion of pulp as slurry is done.
   - Mechanical refining
   - Addition of chemical additive and recycle fibers
9. Paper making machine
   - Moisture in paper is set to be 6-8%.

(a) **Flow Spreader**
(b) **Head Box**
(c) **Fourdrinier Table**
(d) **Press Section**
(e) **Dryer Section**
(f) **Calendar Stock**
(g) **Reel**



PRACTICE EXERCISE

20 mins
Time Yourself

1. The fertility of the soil is improved by
   (a) Rotation of the crops
   (b) Adding lime to the acid salts
   (c) Adding manure and growing legumes
   (d) All
2. Which of the following is incorrect statement about nitrogen importance?
   (a) it enhances plant growth
   (b) it is involved in the synthesis of protein and nucleic acids
   (c) it accelerates fruits and flowers growth
   (d) it is involved in the chlorophyll synthesis
3. The fertilizers, which provide single nutrient from NPK, are called ________ fertilizer.
   (a) straight
   (b) compound
   (c) both a and b
   (d) none of the above
4. Which of the following is macronutrient?
   (a) Cu
   (b) Cl
   (c) H
   (d) Zn
5. Addition of urea to the soil is __________ reaction.
   (a) endothermic
   (b) exothermic
   (c) both a and b
   (d) no heat energy is involved
6. Which of the following is the most suitable catalyst for ammonia synthesis?
   (a) Pt
   (b) $ZnO + Cr_2O_3$
   (c) Fe in fused mixture of $Al_2O_3 + SiO_2 + MgO$
   (d) All of the above
7. The cooling of molten urea by air in the tower is called
   (a) prilling
   (b) evaporation
   (c) condensation
   (d) crystallization
8. Which of the following fertilizers is not useful for paddy rice?
   (a) urea
   (b) DAP
   (c) Ammonium sulphate
   (d) Ammonium nitrate
9. DAP (Diammonium hydrogen phosphate) contains ________ plant nutrients.
   (a) 60%
   (b) 65%
   (c) 70%
   (d) 75%
10. Which of the following potassium fertilizers are more useful for horticultural crops, tobacco & potatoes?
    (a) KCl
    (b) KNO_3
    (c) K_2SO_4
    (d) $KMnO_4$
11. Calcarious material includes
    (a) lime stone
    (b) marble
    (c) chalk
    (d) all of the above

12. Argillaceous material does not include
(a) clay
(b) marine shells
(c) slate
(d) blast furnace slag

13. Which of the following processes is used for the synthesis of cement?
(a) dry process
(b) wet process
(c) both
(d) none

14. Phosphorus helps in the growth of
(a) root
(b) leave
(c) stem
(d) seed

15. How many zones through which the charge passes in a rotary kiln?
(a) 4
(b) 3
(c) 2
(d) 5

16. The nutrients which are required in very small amount for the normal growth of plants are called
(a) nitrogenous fertilizers
(b) micronutrients
(c) phosphorus fertilizer
(d) all of the above

17. Which one of the following set of raw material is most suitable for manufacture of urea?
(a) CH_4, N_2 and CO_2
(b) H_2, N_2 and CO
(c) H_2, CO_2 and H_2O
(d) H_2O, N_2 and H_2

18. Which one of the following statement is correct for urea?
(a) it is a synthetic fertilizer
(b) it is a natural fertilizer
(c) it provides micronutrients to the plants
(d) it is an inorganic water soluble compound

19. The percentage of nitrogen in urea is
(a) 36%
(b) 46%
(c) 56%
(d) 66%

20. Which one of the following is an inorganic fertilizer?
(a) manure
(b) urea
(c) ammonium nitrate
(d) All

21. Which one of the following fertilizers provides the nitrogen and phosphorus to the plant?
(a) urea
(b) calcium superphosphate
(c) diammonium phosphate
(d) potassium nitrate

22. The potassium present in plant, help the plant to
(a) form starch, sugar and fibrous material
(b) ripen the seeds and fruits
(c) increase the resistance against disease
(d) all the above statements are correct

23. Cement is a mixture of
(a) clay and clinker
(b) clay, lime stone and gypsum
(c) lime stone and gypsum
(d) lime stone and clay

24. What is clinker?
(a) roasted calcareous material
(b) roasted argillaceous material
(c) roasted calcareous and argillaceous material
(d) roasted gypsum

25. Cement is a mixture of so many compounds roasted in rotary kiln. Which substances has greater percentage?
(a) Lime (CaO)
(b) Silica (SiO_2)
(c) Alumina (Al_2O_3)
(d) Magnesia (MgO)

26. Which one of the following raw material is not present in the cement?
(a) lime stone
(b) gypsum
(c) KNO_3
(d) iron oxide

27. Which sequence of steps is correct for the manufacture of cement?
(a) crushing, heating, mixing, grinding
(b) crushing, mixing, heating, grinding and mixing
(c) crushing, grinding, mixing, heating
(d) mixing, heating, grinding, crushing

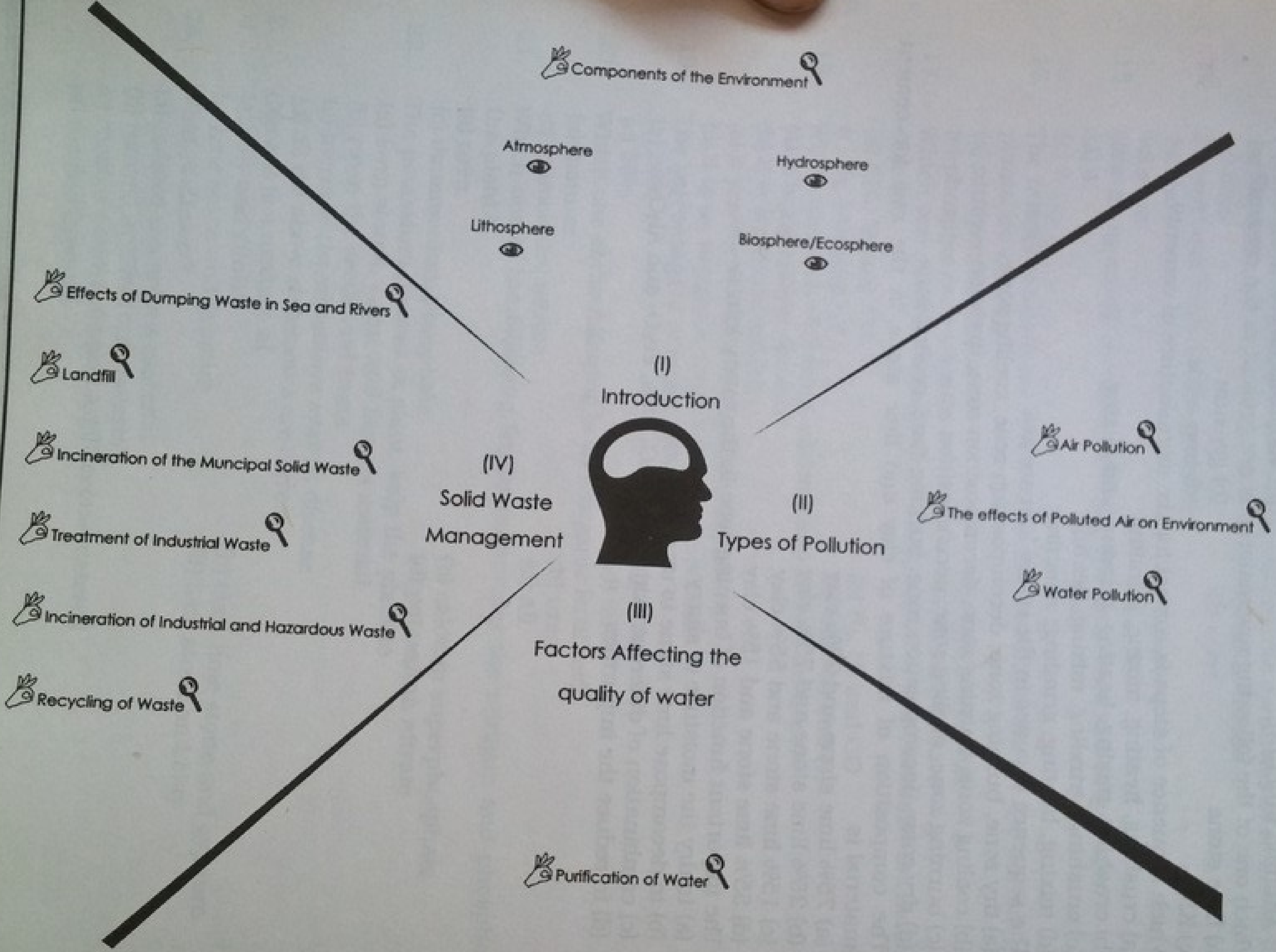
28. The sequence of zones in the rotary kiln are as
(a) dry zone, burning zone, decomposition zone, cooling zone
(b) cooling zone, burning zone, decomposition zone, dry zone
(c) burning zone, cooling zone, decomposition zone
(d) dry zone, decomposition zone, burning zone, cooling zone

29. The composition of mixture of clay and lime stone in the raw for cement material is
(a) 75% lime stone and 25% clay
(b) 25% lime stone and 75% clay
(c) 15% lime stone and 55% clay
(d) 55% lime stone and 15% clay

30. The important function of burning zone in the rotary kiln is
(a) to dry the moisture of slurry
(b) to decompose lime stone to unslaked lime
(c) combination of different oxides like CaO, SiO_2, Fe_2O_3 and Al_2O_3
(d) to reduce the impurities

Chapter 16

ENVIRONMENTAL CHEMISTRY



(I) Introduction

- Components of the Environment
  - Atmosphere
  - Hydrosphere
  - Lithosphere
  - Biosphere/Ecosphere

(II) Types of Pollution

- Air Pollution
- The effects of Polluted Air on Environment
- Water Pollution

(III) Factors Affecting the quality of water

- Purification of Water

(IV) Solid Waste Management

- Effects of Dumping Waste in Sea and Rivers
- Landfill
- Inceneration of the Muncipal Solid Waste
- Treatment of Industrial Waste
- Incineration of Industrial and Hazardous Waste
- Recycling of Waste

ENVIRONMENTAL CHEMISTRY

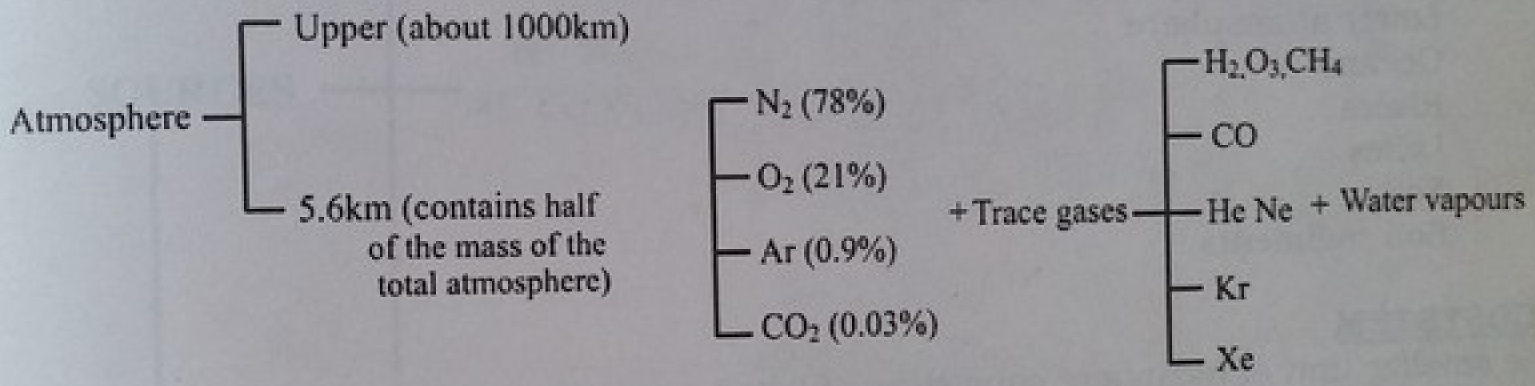
The branch of chemistry that deals with the abnormalities in the environment and their adverse effects on humans beings is called environmental chemistry. This branch is related to the other sciences like physics, medicine, biology agriculture, public health and sanitary engineering etc.

COMPONENTS OF THE ENVIRONMENT

(i) Atmosphere
(ii) Hydrosphere
(iii) Lithosphere
(iv) Biosphere (Ecosphere).

Atmosphere

1000km thick gaseous layer above the surface of earth is called atmosphere.



Function/Advantage

(i) These gases in atmosphere absorb the harmful radiation like cosmic rays, electromagnetic radiations coming from the sun.
(ii) Maintains heat balance of the earth.
(iii) Gases are essential for sustaining life on earth.
O_2 – Breathing
N_2 – nitrogen fixing bacteria
CO_2 – photosynthesis
Moisture – moistening / freshness

Hydrosphere

It includes water bodies
1- Oceans – 97%
2- Polar ice caps - 2%
3- Fresh water 1% (used as)
    69% - Agriculture
    23% - Industry
    8% - Domestic
4- Rivers
5- Lakes
6- Streams
7- Ground reserves

Lithosphere

It consists of rocky crust of earth extending 1000km deep. It has two parts
(i) Mantle (ii) Core

Most of the mass is composed of eleven elements (95.5%).

O_2	46.6%
Si	27.72%
Al	8.13%
Fe	5%
Ca	3.63%
Na	2.83%
K	2.59%
Mg	2.09%
Ti, H_2 & P	less than 1%
Trace elements	0.1-0.02%

Biosphere

The region of earth capable of supporting life. It includes :-

Lower atmosphere
Oceans
Rivers
Lakes
Soil
Soil sediments

ECOSYSTEM

The smaller unit of biosphere consisting of living organism i.e. plant, animal, microbes and human beings; their interaction with environment that depend on the physical factors such as soil, water and air.

Environmental Pollutant

Any substance that adversely affects the human health, quality of life and the natural functioning of the ecosystem.

Causes of Environmental Pollution:-

The main factors which adversely and rapidly affect the human health and ecosystem are due to the following reasons.

- Rapid growth in population
- Urbanization
- Industrialization
- Transportation

Type of Pollutants

- Primary pollutant
- Secondary pollutant

Primary Pollutants

The waste products coming from the chimneys of the industrial units and exhaust of automobiles are called primary pollutants e.g.

SO_x (SO_2, SO_3)
CO_x (CO, CO_2)
NO_x (NO, NO_2)
HC, NH_3, Fluorides
Radioactive material

Secondary Pollutants

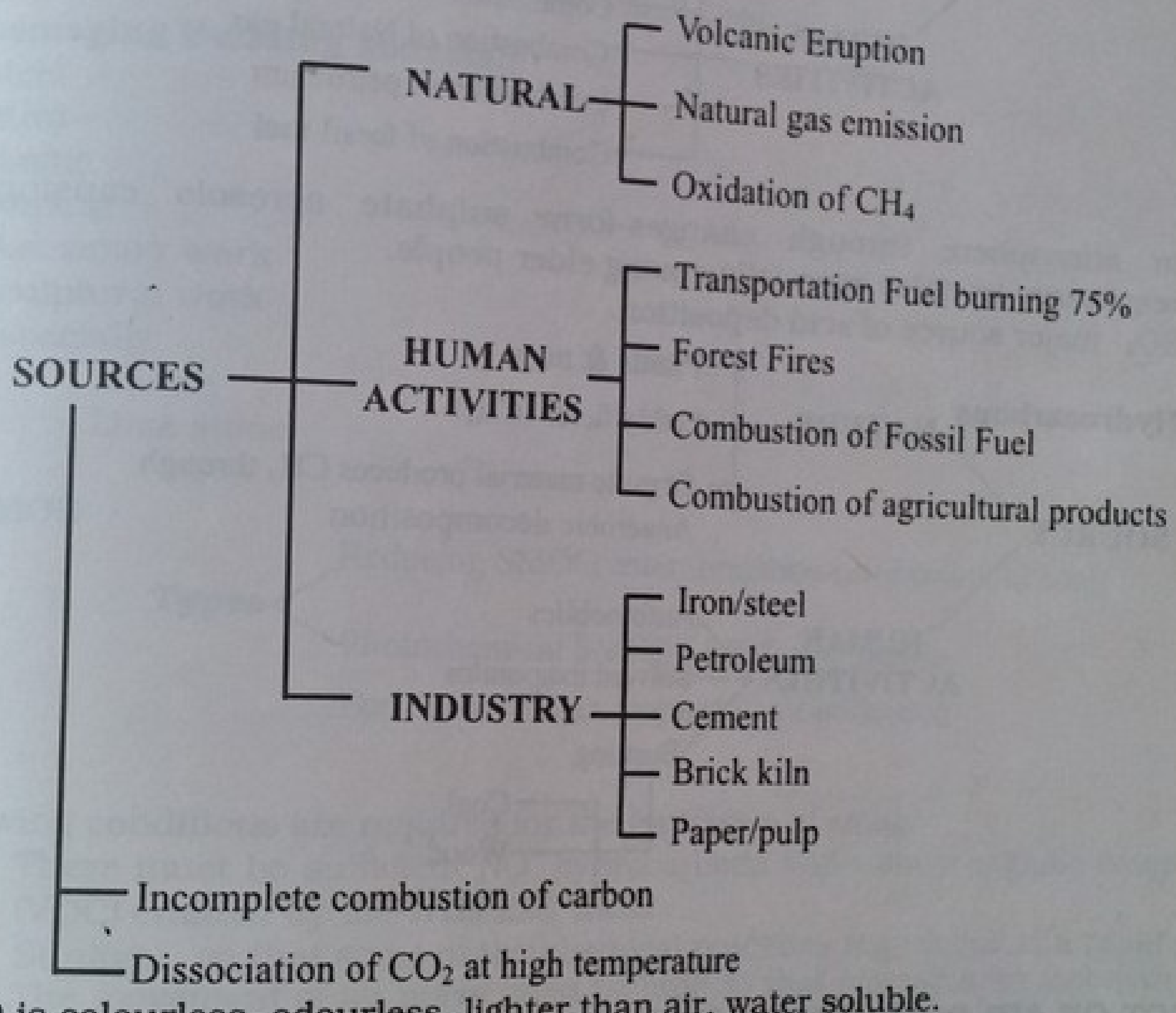
The primary pollutants in the atmosphere through various reactions produce the products called secondary pollutants.

H_2SO_4, N_2O, H_2CO_3, HF peroxyacetyl-nitrate (PAN) O_3. Aldehydes, ketones peroxybenzol.

SOURCE OF MAIN PRIMARY AIR POLLUTANTS

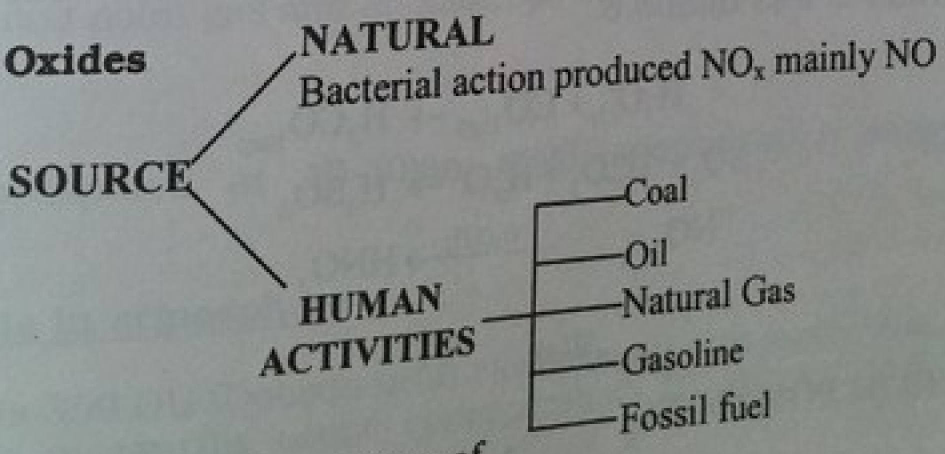
CO_x, SO_x, NO_x, HC

1- Carbon Monoxide


SOURCES
NATURAL
Volcanic Eruption
Natural gas emission
Oxidation of CH_4
HUMAN ACTIVITIES
Transportation Fuel burning 75%
Forest Fires
Combustion of Fossil Fuel
Combustion of agricultural products
INDUSTRY
Iron/steel
Petroleum
Cement
Brick kiln
Paper/pulp
Incomplete combustion of carbon
Dissociation of CO_2 at high temperature

- CO is colourless, odourless, lighter than air, water soluble.
- **Toxic:-** It binds with Haemoglobin strongly, no more transportation of O_2 causing headache, fatigue, unconsciousness eventually death. Its antidote is high-pressure O_2.

2- Nitrogen Oxides



- In the atmosphere residence time of
  NO – 4 days and NO_2 – 3 days

- Photochemical reaction converts NO_x into HNO_3
  Which is carried down in either rainfall or as dust.

3- **Sulphur Oxides**

- SOURCE
  - NATURAL
    - From volcanoes (67%) on global scale
    - Decomposition of organic matter containing gases
  - HUMAN ACTIVITIES
    - Combustion of Coal
    - Combustion of Crude Oil
    - Combustion of Natural gas
    - Combustion of petroleum
    - Combustion of fossil fuel

- In atmosphere through changes-form sulphate aerosols causing severe respiratory troubles especially among elder people.
- SO_2- major source of acid deposition.

4- **Hydrocarbons**

- SOURCE
  - NATURE
    - Plants & trees
    - Paddy fields (CH_4)
    - Organic material produces CH_4 through Anaerobic decomposition
  - HUMAN ACTIVITIIES
    - Automobiles
    - Solvent evaporator
    - Burning
      - Coal
      - Wood
      - Petroleum

EFFECT OF AIR POLLUTANTS/POLLUTED AIR ON ENVIRONMENT

1- ACID RAIN

Discovered by Angus Smith 1650, a serious environment problem in 1950's, initially referred as precipitation, which is more acidic than natural rain because pH of unpolluted rain water is less than 5.6.

$$H_2O_{(l)} + CO_{2(g)} \rightarrow H_2CO_{3(aq)}$$

$$SO_2 + 1/2O_2 + H_2O \rightarrow H_2SO_4$$

$$NO_2 \xrightarrow{H_2O,O_2} HNO_3$$

- ACID DEPOSITION
  - Wet
  - Dry

ACIDIFICATION
- Rock
- Soil
- Buildings

Al
Mg
Pb
Ca

Water bodies taken by fish accumulate them.
Al-cause clogs in the gills thus causing suffocation.

- **Acidification of Soil**
  Leach nutrients
  Damaging
    - Leaves
    - Plants
    - Growth of forest

- **Damaging Building Materials**
  Steel
  Paint
  Plastic
  Cement
  Massonary work
  Sculptural work
  Especially
    Marble
    Lime stone

2- **SMOG**

Types
- Reducing SMOG enter formation-combustion of coal.
- Photochemical SMOG / Oxidizing SMOG
  Formation. Water droplets + Air pollutants

The following conditions are required for the formation of smog.

1- There must be sufficient NO, hydrocarbons and volatile organic compounds (VOC) emitted by the vehicular traffic.
2- Sunlight, so that some of the chemical reactions may occur at a rapid rate.
3- The movement of air mass must be little so that reactions are not disturbed.

OZONE

Atmosphere

Ozone is low boiling point gas and an allotrope of oxygen.

Presence

Just above troposphere at 15-40km most concentration ranges 25-28km in stratosphere.

Amount of Ozone in atmosphere

Normal amount is 350 DU (Dobson unit) closer to equator lesser than 350U. The most common unit for measuring ozone concentration DU after G.M.B Dobson, the 1st scientist to investigate atmosphere.

Production

In tropical region usually in mesosphere

$$O_2 \xrightarrow{\text{Dissociates}} O+O$$

$$O+O_2 \rightarrow O_3$$

that diffuse down in stratosphere from mesosphere.

Function

Filter the harmful radiation of sunlight like UV.

Depletion of Ozone

Over Antarctic, in 10 years (1970s-1980) times has shown 50% depletion of overhead ozone layer. The region in which ozone depletes substantially every year during Sep-Nov is termed as "Ozone hole". This occurs due to various chemical reactions worldwide.

Role of CFCs in Destroying Ozone

CFCs used as refrigerants in air conditioners or in aerosol sprays. CFCs diffuse from troposphere to stratosphere and form free radical due to UV radiations.

$$CFCl_3 \xrightarrow{UV} CFC\dot{l}_2 + C\dot{l}$$

$$C\dot{l} + O_3 \rightarrow Cl\dot{O} + O_2$$

$$Cl\dot{O} + O \rightarrow C\dot{l} + O_2$$

One Cl can destroy 100,000 molecules of O_3.

Effect of O_3 as Pollutant

Health problems
Damages eyes
Decreases the elasticity of lung tissues
Aggravates ASTHMA, Coughing, Chest Discomfort

Plants and other materials

- Attacks rubber
- Reduces
  - Durability
  - Appearance of paint
- Causes
  - Fabric dyes to fade

REQUIREMENT OF PURE WATER

Pure water is essential for life. A healthy man uses average 1.5dm³ of free drinking water per day. All living organism contain water e.g. an adult 60% and child 70% of the body weight. Marine life is impossible without water.

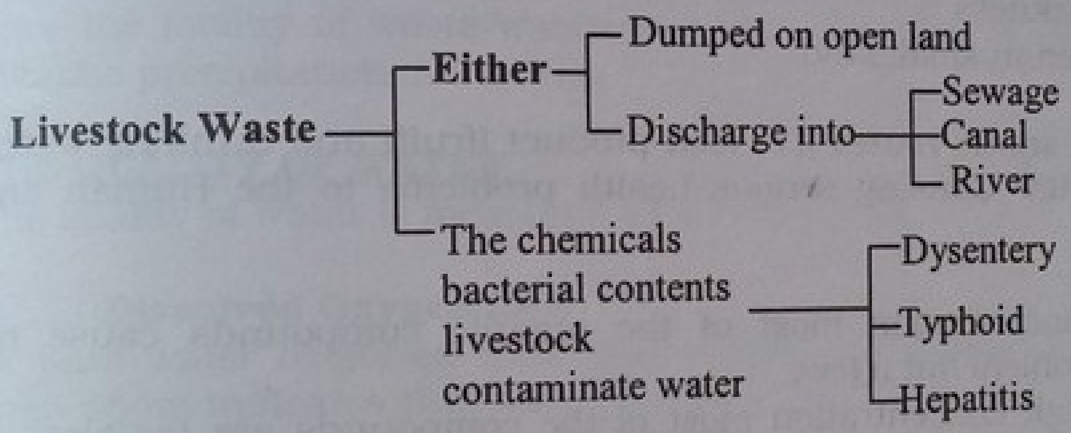
Source

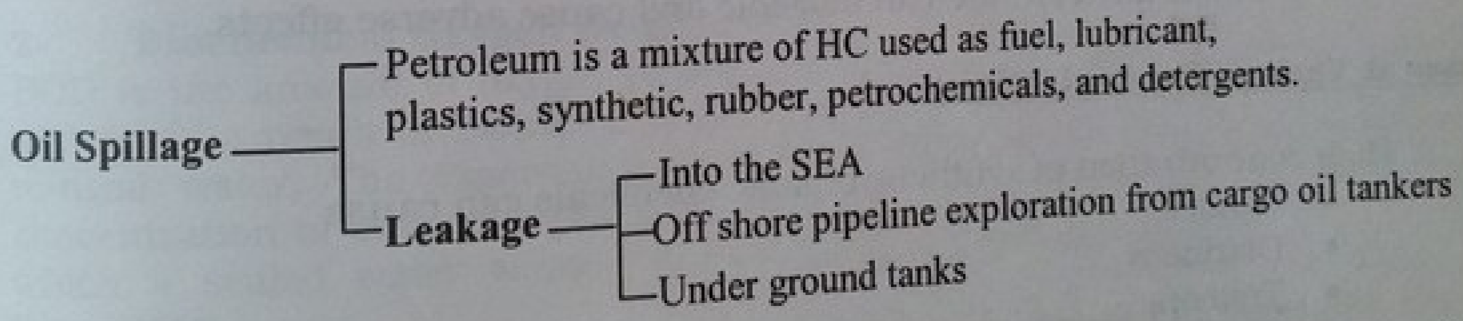
Surface and ground fresh water are the main sources of water.

Human Activities Causing Water Pollution

The following human activities may result in the contamination of surface and ground water.

- Livestock waste
- Oil spillage
- Detergents
- Pesticides
- Disposal of industrial waste
- Leather tanneries
- Water bodies
- Septic tanks
- Mining
- Petroleum and natural gas production




Oil Spillage
Petroleum is a mixture of HC used as fuel, lubricant, plastics, synthetic, rubber, petrochemicals, and detergents.
Leakage
Into the SEA
Off shore pipeline exploration from cargo oil tankers
Under ground tanks

Many petroleum products are poisonous and pose serious health problems to human animal and aquatic life.

(i) Polycylic aromatic HC are carcinogenic even at low concentration.
(ii) Soluble aromatic fractions of oil (C_{10} or less) affect the marine organism – causing death.
(iii) Oily surface layer.
  - No transmission of light no photosynthesis.
  - Dissolved Oxygen in water is decreased.

Detergent

- Excessive use of the detergent in household and industry causing water pollutant as follow.

- In sea/river greatly affects the aquatic life.
- Upsets the ecological balance of aquatic bodies
- Mobilize the toxic ions (Pb, Cd, Hg) from the sediments into water.

Pesticides

More than 10,000 different types of synthetic pesticide (pests) harm the crops and transmit diseases to the human and animals both.

Types

(i) Insecticides (Kill insects)
(ii) Herbicides (Kill undesired growth/plants)
(iii) Fungicides (Controls the growth of fungus)

Advantages

- Pesticides are used to eradicate diseases such as
  - ➢ Malaria
  - ➢ Yellow fever
  - ➢ Bubonic plaque
  - ➢ Sleeping sickness
- Better production even in small land.

Disadvantages

(i) Enters from the various routes (i.e. food product (fruit) and drinking water) into the food chain. Causing serious health problems to the Human and animals.

(ii) No Safe levels
- In low concentration most of the organic compounds cause no serious problem but a few.
- At even high concentration most of the compounds are tasteless & odourless.
- Chlorinated HC are carcinogenic and cause adverse effects.

Diseases at Various Concentrations

(i) High concentration of synthetic organic chemicals can cause
- Nausea
- Dizziness
- Tremors
- Blindness

(ii) At low concentration these compounds become tasteless and odourless, they may develop:-
- Skin eruption
- Central nervous system impairment

(iii) Still lower concentrations when ingested over months or years cause health problems or cancer.

Industrial Waste Effluents

Chemical industries i.e. leather tanneries, fertilizer, oil refining, petrochemical, textile, paper pulp, paper board, rubber, agrochemicals are always accompanied by some:-

- **By Products**
  - Waste heat
  - Smoke
  - Solid waste
- **Waste effluents or Pollutants**
  - Highly toxic synthetic O.C
  - Oil, grease/mineral acid
  - Heavy metals like Pb, Sb, As, Cd, Cr, Hg,..... When ingested causing
    - Anemia
    - Kidney disease
    - Nervous disorder
    - High blood pressure

Leather Tanneries

Leather tanning units from cottage scale to big industrial units use chromium (VI) salt for leather tanning. The effluents are discharged into (open land and sewage system). Cr (VI) highly toxic and is known to cause cancer. Only some leather tanning units have the facility of waste water treatment by reducing Cr(VI) into Cr(III) followed by alkaline precipitation of $Cr(OH)_3$.

THE QUALITY OF WATER

The quality of water is measured as DO, BOD and COD.

1- Dissolved Oxygen (DO)

In pure water dissolved molecular oxygen ranges from 4-8ppm. The DO value less than 4ppm indicates that water is polluted because the organic matter used up DO or oxidized with DO.

2- Biochemical Oxygen Demand (BOD)

BOD is the amount of oxygen consumed in the sample containing dissolved organic matter as a result of biological oxidation reaction. Catalyzed by micro organisms in natural water. The experiment is carried out within a period of five days. The concentration of oxygen is calculated at the beginning and at the end of five days in which a sealed water sample is maintained in dark at constant temperature of 20 or 25°C.

Conclusion:- Higher value of BOD will indicate more pollution.

3- Chemical Oxygen Demand (COD)

COD is a direct measurement of chemically oxidizable organic matter in water higher value of COD means more pollution.

COD is determined directly by treating water (sample) with dichromate ions $Cr_2O_7^{-2}$ powerful oxidizing agent). The organic matter in the water is oxidized while the remaining dichromate is determined titremetrically.

PURIFICATION OF WATER

We use ground water or surface water., ground water is usually more clean than surface water the surface water is contaminated and requires treatment to make it POTABLE i.e. safe for human consumption. The treatment is carried out in variou stages i.e. aeration, coagulation and chlorination.

Chapter 16 Environmental Chemistry

1- Aeration

The quality of raw water is improved by aeration. For this air is passed through raw water.

Air (Aeration)

- Removes the foul smelling H_2S
- Organo sulphur compound
- Volatile organic compounds
- Some organic compounds oxidized →CO_2
- Remaining organic compounds are removed by passing water over activated carbon
- Oxidizes soluble Fe^{2+} to Fe^{3+} as $Fe(OH)_3$ which is removed as solid.
- Improves the oxygen level of raw water.

2- Coagulation

The suspended or colloidal forming particles are removed by coagulation. For coagulation we use $Al_2(SO_4)_3$ or alum producing gelatinous $Al(OH)_3$ 80% suspended particles adsorb on the surface of $Al(OH)_3$ and are removed.
Ca^{2+}/Mg^{2+} ions cause hardness which are removed by clark or ion exchange method. Ferric salts can also be used in place of alum but difficult to handle as Fe_2O_3 insoluble exist in the range of pH 3.0 to 13.0.

$$K_2SO_4.Al_2(SO_4)_3.24H_2O+Ca(OH)_2 \rightarrow 3CaSO_4+2Al(OH)_3+24H_2O$$

3- Water disinfections by Chlorine

Disinfections by chlorine is inexpensive and very effective in killing pathogens which may cause

- Cholera
- Typhoid

Harmful effects of chlorinated water are as follow:-

- Chlormated water contains (HOCl) reacts with organic matter or NH_3 producing:-
  - NH_2Cl
  - $NHCl_2$
  - NCl_3 – is powerful eye irritant

$$NH_3+3HOCl \rightarrow NCl_3+3H_2O$$

  The alkaline pH can prevent formation of NH_2Cl.
- Chlorinated water with organic material forms toxic organic compound. e.g.
  (i) Phenol – chlorinated phenol which is toxic having offensive (odour and taste)
  (ii) HOCl reacts with organic matter (humic acid) forming.
  $CHCl_3$
    - Suspected liver carcinogen
    - Negative reproduction
    - Negative development
- Chlorinated water may increase the risk of blade and rectal cancer.
- To avoid toxic compound formation with **Cl_2 , O_3 or ClO_2** is used for disinfection of water.

The most commonly used disinfecting agent is hypochlorous acid (HOCl). This neutral covalent compound readily passes through cell membrane of microbe and kill them. HOCl is not stable so cannot be stored. It can be prepared by either dissolving. Cl_2 gas or sodium and calcium hypochlorite in water having advantage over transporting Cl_2 cylinders.

$$Cl_2 + H_2O \rightarrow HOCl + H^+Cl^-$$

SOLID WASTE MANAGEMENT:

The disposal of domestic refuse, commercial and industrial solid wastes or semisolid materials are studied under the title solid waste management. Effects of Dumping Waste in Sea and Rivers. The dumping of waste materials acids, refinery wastes, explosives, domestic refuse, garbage and radioactive waste in water has damaged the marine environment and caused health hazards to human beings.

Landfill

The municipal solid waste is mainly disposed off by dumping it in a landfill. The landfill is a large hole in the ground or even a bare piece of land. When the landfill becomes full with waste it is covered by soil or clay. The ground water which seeps in the landfill and liquid from the waste itself, all percholate through the refuse producing **leachate**. The leachate contains dissolved, suspended and microbial contaminants.

The gases which are produced in landfills from the waste are methane, ammonia, hydrogen sulphide and nitrogen. The leachate contains volatile organic acids such as acetic acid and various fatty acids, bacteria, heavy metals and salts of common inorganic ions such as Ca^{2+}. The micro-pollutants present in municipal solid waste include common volatile organic compounds such as toluene and dichloremethane.

Incineration of the Municipal Solid Waste

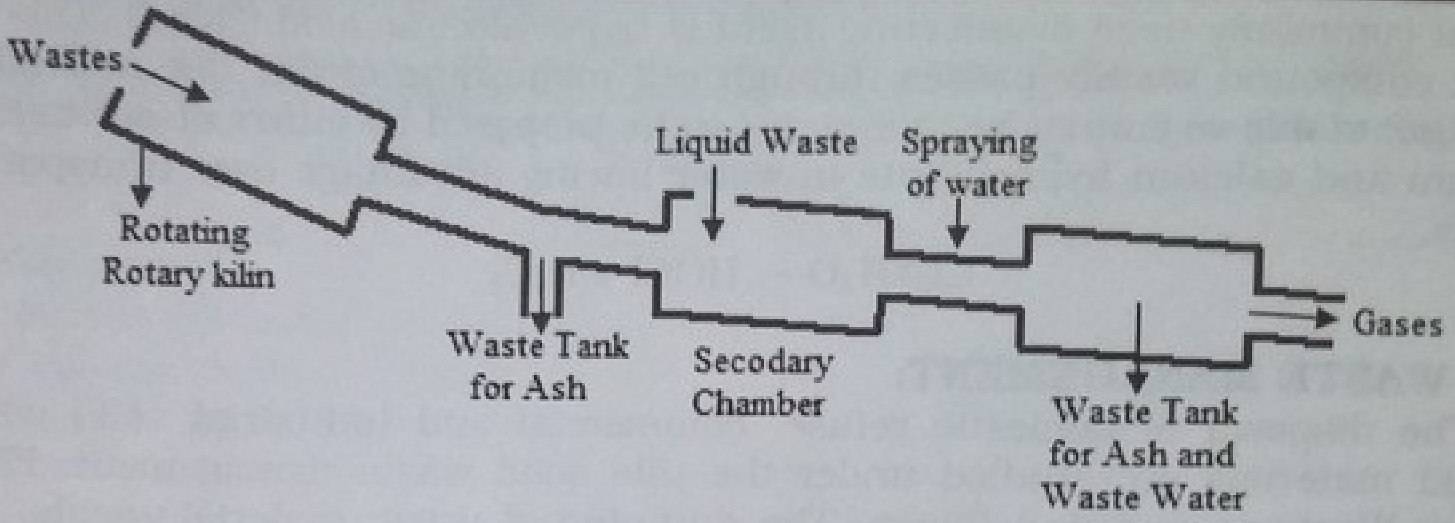
Incineration is waste treatment process in which solid waste is burned at high temperatures ranging from 900 to 1000°C. The burning of the solid waste in the incinerator consumes all combustible materials leaving behind the non-combustible materials and the ash residues. The ash residues of the incinerator are disposed off on the land or landfills. The incineration may reduce the volume of the waste by the two third. In incineration heat of combustion may be used in producing steam which runs the turbines to produce electricity.

Treatment of Industrial waste

The industrial and hazardous wastes are disposed off in landfill or the waste is first incinerated and the residual ash is then disposed off in the landfill. So that the leachate does not contaminate soil and ground water around.

Incineration of Industrial and Hazardous Waste

A general process of high temperature incineration system consists of a rotary kiln which accepts all types of wastes including liquid, solid or sludge.



Although the volume of solid waste is reduced to a much lesser exten burning it in the incinerator, it is not a clean process. Incineration of the solid was a significant source of dioxins which is a class of **carcinogen** compounds. Sm stacks from incineration may emit oxides of nitrogen and sulphur which lead to rain. Heavy metals such as lead, cadmium, mercury, etc. may also be present in leachate of the incinerators.

Recycling of Waste

In recycling some of the used or waste materials are not discarded after t initial use but are processed so that they can be used again. The purpose of recyc is to conserve sources such as raw material and energy. The volume of the wast also much reduced by recycling of the materials. The most common dome materials that are recycled are paper, plastic, glass and aluminium.

The largest item which is recycled is newspaper. In recycling process the fibr the newspaper becomes shorter so it can be recycled again and again for **five times**

The recycling of plastics is done by **reprocessing, depolymerization** **transformation**. In reprocessing the used plastics are remelted and used for smanufacturing of different products e.g. the original use of polystyrene is for manufacturing of foam, packaging, cutlery, furniture, etc. but after its reprocessin is used mostly for the manufacturing of toys, trays, etc. the depolymerization i process in which the used plastics are converted back into their original compone by a chemical or thermal process so that these can be subsequently polymerized ag e.g. polyethylene terephthalate can be thermally depolymerized in the presence o catalyst and heat into its original components. The transformation is a process which used plastics are converted into low quality substances which are later used the production of other materials e.g. cracking of polyethylene at high temperatu gives its monomers which are used for the manufacturing of lubricants.

Chapter 16

Environmental Chemistry

PRACTICE EXERCISE

20 mins
Time Yourself

1. Which of the following is not a heavy industry?
(a) iron
(b) fertilizer
(c) paper
(d) none

2. Which of the following is a macronutrient?
(a) boron
(b) iron
(c) copper
(d) carbon

3. Requirement of macronutrient per acre of the land is
(a) 5 to 200kg
(b) 20-200kg
(c) 200-400kg
(d) 30-400kg

4. Three elements needed for the healthy growth of plants are
(a) N,P,K
(b) N,K,C
(c) N,S,P
(d) N, Ca, P

5. Which of the following is not a secondary pollutant
(a) ozone
(b) carbonic acid
(c) sulphuric acid
(d) carbon dioxide

6. Residence time of methane in the atmosphere is
(a) 3 – 7 days
(b) 2 – 3 days
(c) 3 – 7 years
(d) 2 – 3 years

7. Major cause of SO_2 on global scale is
(a) volcanoes
(b) electric sparks
(c) combustion
(d) all

8. Hypochlorous acid is used for disinfecting the water, it reacts with the dissolved ammonia producing
(a) NH_2Cl
(b) $NHCl_2$
(c) NCl_3
(d) all of the above

9. Acid present in acid rain may be
(a) H_2SO_4
(b) HNO_3
(c) both a and b
(d) none

10. The yellow colour in photochemical smog is due to presence of
(a) dinitrogen oxide
(b) nitrogen dioxide
(c) chlorine gas
(d) chlorine dioxide

11. Which of the following is not a condition for the formation of smog?
(a) sufficient NO
(b) sunlight
(c) less movement of air
(d) winds

12. Incineration of muncipal waste is carried out in the temperature range of
(a) 250 to 500°C
(b) 500 to 900°C
(c) 950 to 1300°C
(d) 900 to 1000°C

13. In which of the following layer of atmosphere, there is more thickness of ozone layer?
(a) troposphere
(b) stratosphere
(c) mesosphere
(d) photosphere

14. Which of the following is not primary pollutant
(a) SO_3
(b) CO
(c) NO
(d) H_2SO_4

15. Which of the following air pollutants is more dangerous for ozone layer?
(a) CFC
(b) CO_2
(c) CO
(d) Oxides of nitrogen

16. Which of the following gases is the main cause of acid rain?
(a) CO
(b) NO_2
(c) both a & b
(d) none of the above

17. Which statement is wrong?
(a) the amount of ozone layer is greater in the region close to the equator
(b) ozone acts as filter for UV radiations
(c) in the equatorial region, it acts as pollutant
(d) CFCs play effective role in removing O_3 in the stratosphere

18. Which of the following factors help to measure quality of water?
(a) DO
(b) BOD
(c) COD
(d) All of the above

19. In the purification of portable water, the coagulant used is
(a) alum
(b) nickel sulphate
(c) copper sulphate
(d) barium sulphate

20. Newspaper can be recycled again and again how many times?
(a) 2
(b) 3
(c) 4
(d) 5

21. The main pollutant of leather tanneries in the waste water is
(a) chromium III
(b) chromium IV
(c) chromium V
(d) chromium VI

22. A single chlorine free radical can destroy how many ozone molecules?
(a) 10
(b) 100
(c) 10000
(d) 100000

23. Which substance can be used for disinfecting water?
(a) $KMnO_4$
(b) Alums
(c) Ozone
(d) All

24. Chlorination of water may be harmful if the water contains
(a) Ammonia
(b) Dissolved oxygen
(c) Carbon dioxide
(d) All

25. Which one of the following makes the bulk of hydrosphere's content?
(a) oceans
(b) glaciers & icecaps
(c) fresh water lakes and ponds
(d) All have equal distribution

26. Which of the following is used as water disinfectant to avoid the formation of toxic compounds
(a) Cl_2
(b) O_3
(c) ClO_2
(d) both b & c

27. The percentage of suspended solid waste in raw water is removed by coagulation is
(a) 60
(b) 70
(c) 80
(d) 90

28. Ozone hole is substantial depletion of ozone in every year during
(a) Aug – Nov
(b) Sep - Nov
(c) Nov – Dec
(d) Dec – Jan

29. The main product of bacterial action is
(a) NOx
(b) NO_2
(c) N_2O_3
(d) NO

30. Pollutants have adverse effect over
(a) Biosphere
(b) Ecosystem
(c) Both a & b
(d) Hydrosphere

SAMPLE PAPER FOR MCAT/ECAT

Note:- Chemistry paper of ECAT contains 30 questions while MCAT contains 60 questions, so extra questions have been added in the sample paper.

(1) All the following variables are used to describe gases except
(a) pressure
(b) volume
(c) moles
[✓ (d) density]

(2) In the van der Waal's equation: $(P + n^2a / v^2)(v - nb) = nRT$ which of the following statement is not true?
(a) n^2a/v^2 correct for the intermolecular forces.
(b) nb correct for the volume occupied by gas molecules.
(c) at high densities, the equation reduces to the ideal gas law.
(d) all of the above statements are correct.

(3) Methyl alcohol is not used as
(a) a solvent
(b) an anti freezing agent
[✓ (c) a substitute for petrol]
(d) for denaturing of ethyl alcohol

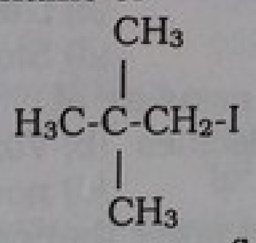
(4) The inhaled breath of diabetics patient contain acetone. A medical student wishes to test for diabetes by asking patient to bubble their breath through a reagent.
[✓ (a) alkaline aqueous iodine]
(b) aqueous bromine
(c) Fehling solution
(d) aqueous NaOH.

(5) Oxygen (molecular weight = 32) diffuses at a rate of $10 cm^3/min$ under the same conditions of temperature and pressure, how fast will hydrogen (molecular weight = 2) diffuse?
(a) $20 cm^3/min$
(b) $40 cm^3/min$
(c) $160 cm^3/min$
(d) $2.5 cm^3/min$

$\frac{r_1}{r_2} = \frac{\sqrt{m_2}}{\sqrt{m_1}}$

$\frac{10 cm^3/min}{x} = 4$

(6) Which is the correct trivial name of



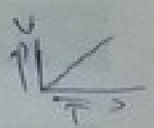
$H_3C-C(CH_3)_2-CH_2-I$

(a) n-pentyliodide
(b)sec-pentyliodide
(c)sec-pentyl iodide
(d)neo-pentyl iodide

(7) When aqueous bromine is added to aqueous phenol a creamy white ppt is obtained. What does this reaction show?
(a) phenol is unsaturated
(b) 2-bromophenol is insoluble in water
[✓ (c) a hydroxy group makes the benzene ring more susceptible to electrophilic attack]
(d) acid-base reaction.

(8) As a substance moves from a solid to a liquid, all of the following changes occur except:
(a) molecules become more disordered.
(b) K.E of the molecules decreases
(c) intermolecular forces become weaker.
(d) molecules move more frequently.

(9) If a graph is plotted between temperature on x-axis and volume on y-axis for 1 mole of gas, then we get straight line, which cuts the temperature axis at.



(a) 0°C
(b) 273.16K
(c) –273.16 K
[✓ (d) –273.16°C]

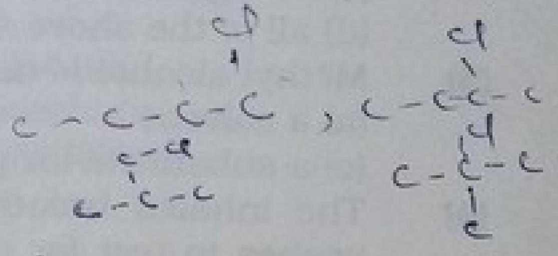
(10) The rectified spirit is
(a)12% alcohol
(b) 90% alcohol
[✓ (c) 95% alcohol]
(d) 100% alcohol

(11) Benzene is a good solvent for.
(a) fats
(b) resins
(c) iodine
[✓ (d) all the above]

(12) Which of the following solids show anisotropy
(a) Plastic
(b) Glass
(c) Rubber
[✓ (d) None of the above.]

(13) Which of the following element doesn`t show allotropy
(a) Carbon.
[✓ (b) Arsenic.]
[✓ (c) Nitrogen]
(d) Sulphur.

(14) Butyl chloride gives possible isomers.
(a) 2
[✓ (b) 3]
[✓ (c) 4]
(d) 5



(15) Purines and pyrimidines are
(a) Enzymes
[✓ (b) Nitrogenous bases]
(c) Carbohydrates
(d) Lipids

(16) Metallic crystals are soluble in
(a) Polar solvent
(b) Non polar solvent
[✓ (c) Fused metal]
[✓ (d) None.]

(17) All the transition elements show.
[✓ (a) Similar physical properties.]
(b) Similar chemical properties
[✓ (c) Both a and b]
(d) None

(18) Paramagnetic behaviour of substance is measured by a balance called
(a) Analytical balance
[✓ (b) Guoy's balance]
(c) Electrical balance
(d) Single beam balance

(19) In solids the temperature is the measure of
(a) Average kinetic energy of molecules
[✓ (b) Vibrational kinetic energy]
(c) Translational kinetic energy
(d) none of the above

(20) Which of the following properties prove that cathode rays are material in nature
(a) they cast shadow
[✓ (b) they possess momentum]
(c) they are negatively charged
(d) all of the above.

(21) Fruit juices and fizzy drinks such as lemonade are often sold in aluminium cans. What is the most important reason aluminium is a suitable metal?
(a) aluminium can be recycled
(b) aluminium has very low density
(c) aluminium is the most abundant metal in the earth crust
[✓ (d) aluminium is resistant to corrosion by organic acids.]

(22) When an electron is moving with velocity of 2.188x10^{6}ms^{-1} in the first orbit of Bohr`s model of hydrogen. The de Broglie wavelength of electron is
[✓ (a) 0.33nm]
(b) 0.34nm
(c) 0.35nm
(d) 0.36nm

$$\lambda = \frac{h}{mv} = \frac{6.63\times10^{-34+31+}}{9.01\times2.18} = 3\times$$

6.63
3
9.89

9.01
2.18
7208
901x
1802xx
19.6918

72.08
7208
901
1802

(23) On heating aldehydes with Fehling's solution, we get a precipitate whose colour is
(a) pink
(b) black
(c) yellow
(d) brick red

(24) When methyl iodide and ethyl iodide are treated with sodium metal, possible major products are obtained.
(a) 1
(b) 2
(c) 3✓
(d) 4

(25) Which of the following rays has greater frequency.
(a) α-rays
(b) β-rays
(c) γ-rays
(d) X-rays

(26) Which statement is consistent with Hund's rule.
(a) Electrons fill orbitals with parallel spins until all the orbitals of the same energy are half filled, then they go into sub-shells with anti-parallel (opposite) spin.
(b) The electrons in the same atom cannot have the same four quantum numbers.
(c) There is maximum of two electrons is an orbital.
(d) None.

(27) What is maximum number of electrons in an orbital with m (magnetic quantum number) =3
(a) 6
(b) 4
(c) 3
(d) 2

m = 1 0 1
l = 2 2(2l+1)

(28) Atomic number of Mn is 25 what is the electronic configuration in the ground state
(a) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^7$
(b) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 4p^5$
(c) $1s^2, 2s^2, 2p^6, 3s^2, 3p^5, 3d^{10}$
(d) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2 3d^5$

(29) Which of the following statement is correct
(a) size of Cl atoms > Cl^- ion
(b) size of Na^+ ion < Na atom ✓
(c) size of Na atom < Na^+ ion
(d) $Cl^- < Na^+$

(30) Which of the following is mineral fibre.
(a) teflon
(b) asbestos
(c) saran
(d) acrylic

(31) Which catalyst is used in contact process?
(a) Fe_2O_3
(b) V_2O_5
(c) SO_3
(d) Ag_2O

(32) The hardest of the following solids is
(a) sodium
(b) diamond
(c) graphite
(d) magnesium

(33) Which of the following elements has greater 1st ionization energy
(a) B
(b) C
(c) N
(d) O

(34) Which of the solid does not contain covalent bond
(a) copper✓
(b) ice✓
(c) diamond
(d) graphite

(35) Which of the following molecule is polar
(a) CCl_4
(b) CO_2
(c) BF_3
(d) none of the above

(36) The balanced chemical equation for the reaction which occurs when Be is added to water is
(a) $Be+2H_2O \rightarrow Be(OH)_2+H_2$
(b) $Be+H_2O \rightarrow Be(OH)_2+H_2$ ✗
(c) $Be+H_2O \rightarrow [Be(OH)_4]^{+2}+H_2$
(d) no reaction ✓

(37) The number of bonds in nitrogen molecule is
(a) one σ one π bond
(b) two σ one π bond
(c) one σ and two π bonds
(d) three σ bonds only

(38) Which of the following theories is superior to others
(a) VSEPR theory
(b) VBT
(c) MOT
(d) none of the above

(39) Which of the following relation is not possible
(a) $\Delta H = \Delta H_1+\Delta H_2+\Delta H_3$
(b) $\Delta E = E_1 + E_2 + E_3$ ✓
(c) $q = q_1+q_2+q_3$
(d) $\sum \Delta H$ (cycle) = 0

(40) Which of the following is not characteristics of reversible reaction
(a) whole amount of reactant does not change into product
(b) chemical equilibrium is established
(c) a catalyst changes the direction of reaction
(d) rate of forward reaction decreases as reaction proceeds

(41) Which of the following points are important in connection with equilibrium constant.
(a) K_C is constant at given temperature
(b) K_C is unaffected by change in concentration of reactants or products
(c) K_C indicates the extent of reaction but not about the rate of reaction.
(d) All of the above

(42) A solution has pH = 0 its H^+ ion concentration is
(a) 1×10^{-1}
(b) 1×10^{-14}
(c) 1×10^{-7}
(d) 1

(43) Solubility of CaF_2 is 2.0×10^{-4} gdm^{-3} then Ksp of CaF_2 is
(a) 4.0×10^{-8}
(b) 3.2×10^{-11} ✓
(c) 2.0×10^{-8}
(d) 4.0×10^{-12}

$Ksp = \cancel{3S}\ 4S^3$
$\frac{2\times10^{-4}}{4} =$
0.5×10^{-4}

(44) 1 mole of electron has mass in microgram.
(a) 1.008×10^{-3}
(b) 5.5×10^{-4} ✓
(c) 1.84×10^{-4}
(d) 1.673×10^{-3}

9.01×6.0
18×10

(45) The unit of molality is
(a) moles dm^{-3}
(b) moles Kg^{-1} ✓
(c) gram dm^{-3}
(d) none

(46) The use of antifreeze in the automobile radiator is an important application of
(a) constitutive property
(b) additive property ✗
(c) colligative property ✓
(d) intrinsic property

(47) A solution can be both
(a) dilute and concentrated
(b) dilute and saturated
(c) saturated and unsaturated
(d) saturated and super saturated.

(48) At which electrode the reduction of the solution is occurring in Al–Ag cell.
(a) Aℓ
(b) Ag ✓
(c) Both
(d) Neither

(49) Consider the following redox reaction.
$Zn+dil\ HNO_3 \rightarrow Zn(NO_3)_2+N_2O+H_2O$
The coefficient number of HNO_3 in the equation is
(a) 6
(b) 8
(c) 10 ✓
(d) 4

(50) In which of the following type of reactions, energy of reactant is greater than energy of product.
(a) endothermic
[✓ (b) exothermic]
(c) unpredictable
(d) same

(51) Which of the following elements react with steam to produce H_2 gas.
(a) Pd
(b) Ni
(c) Sn
[✓ (d) All of the above]

(52) Which of following metals can be displaced by all other metals from its solution
(a) Ag
(b) Aℓ
[✓ (c) Au]
(d) Cu

(53) The unit of the rate constant (k) is same as that of rate of reaction
(a) First order reaction
(b) Second order reaction
[✓ (c) Zero order reaction]
(d) Third order reaction

(54) Which of the elements do not fall in stair case of the modern periodic table
(a) Si
(b) As
(c) Te
[✓ (d) none of the above]

(55) Acid present in acid rain may be
(a) H_2SO_4
(b) HNO_3
[✓ (c) both a and b]
(d) none of the above

(56) Across short period the melting and boiling point increase upto
(a) IIIA group
[✓ (b) IVA group]
(c) VA group
(d) VIA group

(57) Which of the following elements conduct electricity and also melts below 100°C
(a) Aluminium
[✓ (b) Sodium]
[✓ (c) Carbon]
(d) Sulphur

(58) Which of the following is the formula of chrome red.
[✓ (a) Pb_3O_4]
(b) $2PbCO_3 - Pb(OH)_2$
(c) $PbCrO_4 - Pb(OH)_2$
(d) Pb_2O.

(59) The compound which is added to leaded gasoline to save engine from lead oxide and lead sulphate deposits is
(a) Ethylene iodide
[✓ (b) Ethylene bromide]
(c) Ethylene chloride
(d) Ethylene fluoride

(60) Regular coiling or zigzagging of polypeptide through hydrogen bonding is its.
(a) Quantum structure
[✓ (b) Secondary structure]
(c) Tertiary structure
(d) Primary structure

ANSWER KEY

CHAPTER-1

1	A	11	A	21	C	31	C	41	A
2	A	12	D	22	D	32	C	42	C
3	A	13	A	23	C	33	C	43	C
4	A	14	D	24	B	34	B	44	C
5	C	15	C	25	B	35	C	45	A
6	D	16	A	26	D	36	D	46	C
7	A	17	D	27	D	37	D	47	A
8	D	18	A	28	C	38	B	48	B
9	D	19	B	29	B	39	B	49	B
10	D	20	A	30	B	40	A	50	A

CHAPTER-2

1	C	11	D	21	D	31	B
2	C	12	D	22	B	32	B
3	A	13	A	23	A	33	D
4	A	14	C	24	A	34	D
5	C	15	A	25	C	35	B
6	D	16	C	26	C	36	A
7	D	17	D	27	A	37	C
8	B	18	A	28	C	38	C
9	C	19	C	29	B	39	C
10	D	20	C	30	A	40	A

CHAPTER-3

1	C	11	B	21	D
2	B	12	C	22	B
3	A	13	A	23	B
4	A	14	D	24	B
5	B	15	C	25	B
6	D	16	A	26	B
7	A	17	B	27	C
8	C	18	B	28	B
9	C	19	A	29	D
10	D	20	C	30	B

CHAPTER-4

1	B	11	A	21	D
2	A	12	B	22	B
3	B	13	C	23	B
4	B	14	A	24	C
5	A	15	A	25	C
6	D	16	A	26	D
7	D	17	B	27	D
8	A	18	A	28	A
9	A	19	B	29	D
10	D	20	C	30	B

CHAPTER-5

1	C	11	D	21	D
2	B	12	B	22	B
3	D	13	C	23	A
4	A	14	B	24	D
5	D	15	C	25	B
6	B	16	C	26	D
7	A	17	A	27	D
8	D	18	A	28	B
9	C	19	D	29	D
10	B	20	A	30	C

CHAPTER-6

1	B	11	A	21	C
2	D	12	D	22	D
3	C	13	D	23	B
4	C	14	B	24	C
5	D	15	C	25	D
6	B	16	D	26	C
7	A	17	B	27	C
8	C	18	B	28	C
9	B	19	B	29	B
10	D	20	C	30	D

CHAPTER-7

1	A	11	D	21	C	31	D
2	D	12	C	22	B	32	B
3	C	13	A	23	C	33	C
4	A	14	A	24	A	34	D
5	D	15	D	25	D	35	B
6	B	16	C	26	B	36	C
7	C	17	C	27	C	37	C
8	A	18	B	28	C	38	D
9	A	19	C	29	C	39	C
10	B	20	C	30	B	40	C

CHAPTER-8

1	A	11	C	21	C
2	B	12	C	22	D
3	C	13	C	23	B
4	A	14	B	24	C
5	A	15	A	25	C
6	A	16	C	26	C
7	B	17	D	27	C
8	B	18	B	28	B
9	D	19	D	29	C
10	B	20	C	30	C

CHAPTER-9

1	B	11	C	21	C	31	D
2	C	12	B	22	C	32	B
3	B	13	B	23	C	33	B
4	B	14	A	24	B	34	C
5	C	15	C	25	C	35	D
6	D	16	A	26	C	36	D
7	C	17	B	27	C	37	B
8	D	18	C	28	D	38	B
9	B	19	B	29	C	39	A
10	D	20	C	30	D	40	D

CHAPTER-10

1	B	11	C	21	B
2	A	12	D	22	A
3	D	13	D	23	D
4	B	14	D	24	C
5	D	15	B	25	D
6	A	16	C	26	C
7	D	17	A	27	A
8	C	18	B	28	B
9	C	19	C	29	D
10	B	20	A	30	C

CHAPTER-11

1	C	11	C	21	D
2	B	12	D	22	C
3	A	13	C	23	D
4	B	14	D	24	A
5	D	15	A	25	B
6	C	16	A	26	D
7	A	17	C	27	D
8	C	18	D	28	C
9	C	19	C	29	A
10	C	20	C	30	C

CHAPTER-12

1	D	11	A	21	D	31	C
2	C	12	D	22	C	32	D
3	D	13	B	23	C	33	D
4	D	14	A	24	D	34	A
5	B	15	C	25	C	35	D
6	C	16	A	26	C	36	B
7	C	17	D	27	B	37	D
8	D	18	A	28	C	38	A
9	C	19	D	29	C	39	B
10	C	20	C	30	C	40	D

CHAPTER-13

1	D	8	C	15	C	22	B	29	B
2	C	9	A	16	D	23	B	30	A
3	B	10	C	17	A	24	C	31	B
4	B	11	B	18	C	25	C	32	B
5	A	12	C	19	A	26	D	33	C
6	B	13	A	20	D	27	D	34	B
7	A	14	A	21	A	28	A	35	D

CHAPTER-14

1	C	11	D	21	B
2	B	12	B	22	A
3	C	13	D	23	C
4	A	14	B	24	B
5	B	15	C	25	C
6	D	16	A	26	B
7	A	17	D	27	A
8	D	18	C	28	C
9	C	19	C	29	C
10	A	20	C	30	B

CHAPTER-15

1	D	11	D	21	C
2	C	12	B	22	D
3	A	13	C	23	B
4	C	14	D	24	C
5	B	15	A	25	A
6	C	16	B	26	D
7	A	17	A	27	C
8	D	18	A	28	D
9	D	19	B	29	A
10	B	20	C	30	C

CHAPTER-16

1	D	11	D	21	B
2	D	12	D	22	D
3	A	13	B	23	A
4	A	14	D	24	A
5	D	15	A	25	A
6	C	16	B	26	D
7	A	17	A	27	C
8	D	18	D	28	B
9	C	19	A	29	D
10	B	20	D	30	B

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1	D	11	D	21	D	31	B	41	D	51	D
2	C	12	D	22	A	32	B	42	D	52	C
3	C	13	C	23	D	33	C	43	B	53	C
4	A	14	C	24	C	34	A	44	B	54	D
5	B	15	B	25	C	35	D	45	B	55	C
6	D	16	C	26	A	36	D	46	C	56	B
7	C	17	C	27	D	37	C	47	A	57	B
8	B	18	B	28	D	38	C	48	B	58	A
9	D	19	B	29	B	39	B	49	C	59	B
10	C	20	B	30	B	40	C	50	B	60	B

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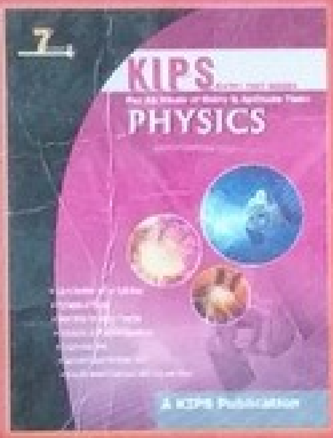

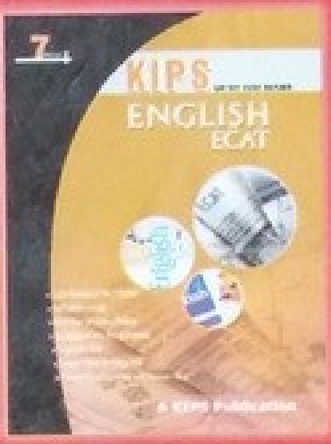

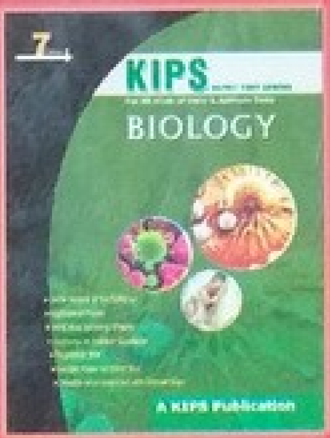

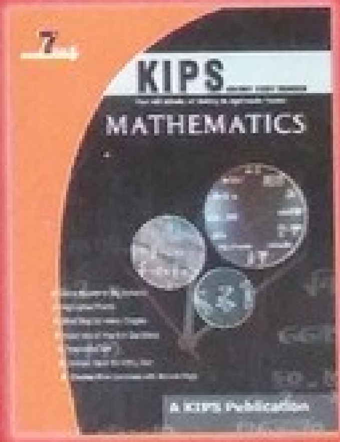

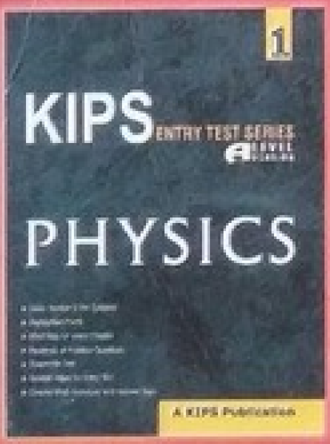

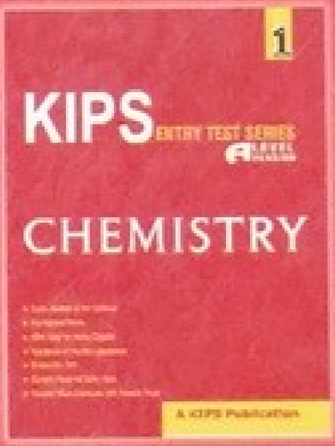

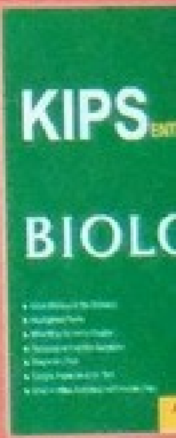

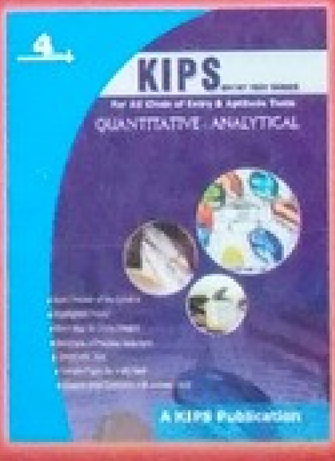

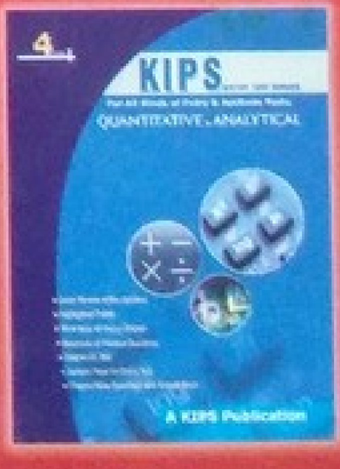

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